# THE GENERATION
AND
# UTILISATION OF COLD

## A GENERAL DISCUSSION

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Reprinted from the *Transactions of the Faraday Society*, No. 53,
Vol. XVIII., Part 2, December, 1922.

# THE GENERATION AND UTILISATION OF COLD.

## *A GENERAL DISCUSSION.*

A GENERAL DISCUSSION on "THE GENERATION AND UTILISATION OF COLD" was held jointly by The Faraday Society and The British Cold Storage and Ice Association on Monday, October 16th, 1922, in the Hall of the Institution of Electrical Engineers, Victoria Embankment, London. The meeting consisted of the following three sessions:

(i) 2.30 to 4.15 p.m., presided over by **Professor Alfred W. Porter, D.Sc., F.R.S., F.Inst.P., President** of the Faraday Society.

(ii) 4.45 to 6.15 p.m.; presided over by **Mr. George Goodsir, J.P., F.R.S.S., President** of the British Cold Storage and Ice Association.

(iii) 7.45 to 9.30 p.m.; presided over by **Mr. James Swinburne, F.R.S., M.Inst.C.E., F.Inst.P., Past-President** of The Faraday Society.

During the intervals demonstrations were given by Messrs. Liquid Air (Limited).

The subject was treated under two headings:—

(i) Laboratory Methods of Liquefaction.

(ii) Industrial Methods of Liquefaction and Practical Applications of Low Temperatures.

**Professor Alfred W. Porter** opened the proceedings with the following general introduction.

# THE GENERATION AND UTILISATION OF COLD.

## *A GENERAL DISCUSSION.*

OPENING REMARKS BY THE PRESIDENT OF THE FARADAY SOCIETY,
ALFRED W. PORTER, D.Sc., F.R.S., F.Inst.P.

We have met together to discuss the questions of the production and utilisation of cold. This is the thirty-second General Discussion which has been arranged under the auspices of the Faraday Society, often in conjunction with others. On this occasion we have associated with us the British Cold Storage and Ice Association, and as President of the Faraday Society I welcome its members to our meeting.

We had looked forward to having with us Professor Kamerlingh Onnes and Professor J. P. Kuenen of Leyden. On the eve of the completion of the arrangements for the meeting, however, science suffered a great loss by the sudden and unexpected death of Professor Kuenen.

He was well known to many in England, and therefore his loss is the more personal. I remember him when he worked at University College with Sir William Ramsay. He was afterwards appointed to be Professor of Physics at Dundee University, and in these connections he made many friends in England. He was best known scientifically for his work on binary mixtures of liquids and vapours. He was taking an active interest in the preparations for this meeting when his untimely death occurred. Professor Onnes, owing to delicate health, is also prevented from coming.

The duty of representing the Leyden Cryogenic Laboratory has therefore fallen upon Professor Crommelin whom we are delighted and honoured in welcoming here. M. Georges Claude of Paris was also expected, but is unable to be present. He has, however, sent a communication which is in print and this will be read for him.

This is not the place to go into detail in regard to the principles of mechanical refrigeration. They are all based upon the fundamental fact that heat will not flow spontaneously from a cold to a hot body: the transference can be effected only by the performance of mechanical work. The most theoretically perfect way of doing this is by a contrivance which passes the working substance through a reversed Carnot cycle of changes. In such a cycle the heat $Q_2$ can be removed from a refrigerated material at temperature $T_2$, and the amount $Q_1$ passed out of the system into a condenser at a higher temperature $T_1$ by the aid of the work, W, required to effect the changes, where

$$Q_1 - Q_2 = W,$$

and

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}.$$

So that the coefficient of performance =

$$\frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}.$$

This value of the coefficient of performance represents, however, the unattainable limit: in practice, even if the Carnot cycle is aimed at, additional work has to be done owing to frictional and other losses and the coefficient of performance is always reduced thereby.

The Carnot cycle requires that the compression and expansion shall take place in a cylinder in much the same way as in a steam engine, but in the reversed sense. In mechanical refrigeration it is found to be more convenient to replace the cylinder expansion by expansion through a throttle or valve. In this expansion less external work is done by the system than in cylinder expansion, and therefore to effect the same change in other respects there is a greater call for supply of external work from elsewhere. If the pressure and volume change from $p_1$ and $v_1$ to $p_2$ and $v_2$ in the expansion the work done is only $p_2v_2 - p_1v_1$, whereas in a cylinder expansion it would have been $\int_1^2 p\,dv$.

The difference is

$$p_2v_2 - p_1v_1 - \int_1^2 p\,dv = \int_1^2 v\,dp.$$

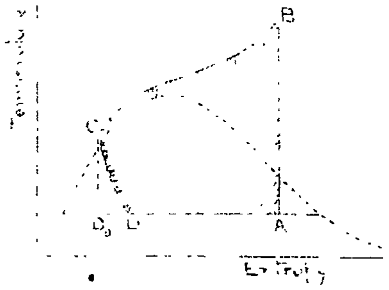

FIG. 1.

I am accustomed to give the name "shirk" to this work that fails to be done; that is,

work actually done + shirk = work that might have been done.

The counting characteristic of the expansion through a throttle is that

internal energy + $pv$ = constant,

or $E + pv$ = constant.

The quantity $E + pv$ is what is usually known in England as Total Heat or Heat Contents. I submit that these names are not satisfactory, because the quantity is not heat in general; and the presence here of a member of the Leyden Laboratory encourages me to press the claims of the name proposed by Kamerlingh Onnes, *viz.*, Enthalpy—a name which I have used for some years. We can denote it by H, which can stand either for capital H (Heat Contents) or for Greek E (Enthalpy) at the option of the reader.

The outline scheme in a $CO_2$ or $NH_3$ machine is as seen in the diagram. The fluid is kept circulating by a compressor pump. The expansion in the throttle is from C to D. The enthalpy does not change in this expansion; neither does it change in any complete cycle. We can write down the following specification of the various changes:—

WITH THROTTLE EXPANSION.

| Path. | Change of Enthalpy. | Heat Entry. | Characteristics. |
|---|---|---|---|
| AB | $H_B - H_A$ | 0 | Cylinder compression |
| BC | $H_C - H_B$ | $H_C - H_B$ | Constant pressure cooling. |
| CD | 0 | 0 | Throttle expansion (adiabatic). |
| DA | $H_A - H_D$ | $H_A - H_D$ | Refrigerating evaporation. |

Hence, Total work done on system = − Total heat entry

$$= -H_A + H_D - H_C + H_B$$

$$= H_B - H_A \text{ because } H_C = H_D.$$

The heat removed from the refrigerated material at the low temperature is $H_A - H_D$. Hence the coefficient of performance is

$$\frac{H_A - H_D}{H_B - H_A}.$$

With cylinder expansion the data are:—

WITH CYLINDER EXPANSION.

| Path | Change of Enthalpy. | Heat Entry. | Characteristics. |
|---|---|---|---|
| AB | $H_B - H_A$ | 0 | Cylinder compression (const. entropy). |
| BC | $H_C - H_B$ | $H_C - H_B$ | Const. press. cooling. |
| $CD_a$ | $H_{D_a} - H_C$ | 0 | Cylinder expansion (const. entropy). |
| $D_aA$ | $H_A - H_{D_a}$ | $H_A - H_{D_a} = Q_2$ | Refrigerating evaporation. |

The coefficient of performance is,

$$\frac{Q_2}{W} = \frac{H_A - H_{D_a}}{H_B - H_A + H_{D_a} - H_D}.$$

because $H_D > H_{D_a}$ and $Q_2 > W$ this expression is greater than for throttle expansion. The adoption of the latter is governed by convenience. I have given these results to show the importance of enthalpy in dealing with refrigeration problems.

Throttle expansion is adopted for convenience, but it is well known that at sufficiently high temperatures it produces heating instead of cooling. This is so for hydrogen and helium at moderate pressures at ordinary temperatures. In such cases pre-cooling is necessary. In the following account we will suppose that the flow is strictly adiabatic. I wish to emphasise, what is not so generally known, that there is in most cases, and probably in all cases, also a *minimum* temperature at which cooling takes place. Such a point has already been experimentally determined for $CO_2$ by Professors Jenkin and Pye.[1] The position found directly lay between − 20·7° and − 31° C. By plotting their data for volume and temperature I calculated in 1913[2] that its value must lie at a temperature not much removed from − 24° C. when the pressure is about half the critical. This result is remarkable, not only owing to its bearing upon the possible use of a throttle at low temperatures but also because it shows that *liquid* $CO_2$ is, in this region, behaving very nearly as a perfect gas—its volume being nearly proportional to the absolute temperature.

Moreover, I had previously shown[3] that all the well-known equations of state concur in indicating that such points should exist. The conclusions to be derived from the various equations are that at any one pressure there are two inversion temperatures if any at all: but that above a certain pressure heating in passing through a throttle is the universal rule at all temperatures. These results are shown in Fig. 2 on which the ordinates are reduced temperatures and the abscissæ are reduced pressures. The curves shown represent the boundary between the heating and cooling regions on various assumptions and from experiment. The change of pressure in going through the throttle is supposed to be small. Curve A is according to van der Waals' equation of state. It would indicate that for a pressure greater than nine times the critical the gas would undergo heating at all temperatures, also that for a reduced pressure of 5 (for example) the gas would cool *only* if the temperature lay between 5·4 and 1·3 times the critical. It does not appear that any substance follows van der Waals' equation however.

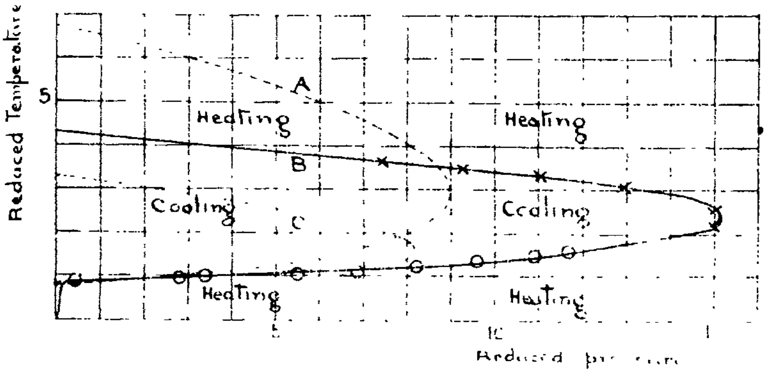

FIG. 2.

Curve A. van der Waals.
" B. Dieterici (modified).
" C. Clausius.
× Inversion points for Nitrogen } from experiment.
o o o " " " $CO_2$ }

Curve C is according to Clausius' equation,

$$\left(\alpha + \frac{3}{\gamma\beta^2}\right)(3\beta - 1) = 8\gamma.$$

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[1] *Phil. Trans.*, 1913, A, No. 499.
[2] *Proc. Roy. Soc.*, A. Vol. LXXXIX., 377.
[3] *Phil. Mag.*, April, 1906, June, 1910.

where $\alpha$, $\beta$, $\gamma$ are the reduced pressure, volume and temperature respectively. Curve B is, according to Dieterici's form of equation, modified as regards the power of $\gamma$ in the index as follows:—

$$\alpha = \frac{\gamma}{2\beta - 1} \exp. \left[ 2\left(1 - \frac{1}{\gamma^n \beta}\right) \right].$$

where $n$ is taken as 5/3. On the same curve are shown inversion points for nitrogen (crosses) and for carbon dioxide (small circles) obtained from Amagat's data of $p_1 \, v_1 \, T$ for these gases by making use of the fact that at an inversion temperature (at which heating changes to cooling or *vice versa*) $T\frac{\partial v}{\partial T} - v = 0$. These experimental values lie *almost precisely on the curve calculated from Dieterici's equation with its modified index*. The cooling and heating regions for these real cases are labelled in the diagram. These results can be trusted for points above the critical point, but for lower temperatures and high pressures, Dieterici's equation is not valid.

It will be perfectly clear from the above that no such law as the inverse square temperature law for the cooling coefficient can possibly be valid in general. The true law may change sign twice or not at all.

These facts may not have any importance in connection with food refrigeration, because the working substances selected will always be such as at ordinary temperatures are either below or at least in the neighbourhood of their critical temperatures; but they do impose a limit to the lowest temperature attainable by throttle expansion.

A further word of explanation may be useful. The fall of temperature in throttle expansion is to be reckoned between any two points (one on each side of the throttle) at which the velocity of flow is small. In the throttle valve itself very high velocities may be reached, and since a considerable amount of energy is then present as kinetic energy the temperature may fall *in the throttle* below the final temperature. Ordinary hydrodynamics shows that if there were no friction in the gas the quantity $-\int v\,dp$ would be transformed into kinetic energy, ultimately being re-transformed as the passage gets wider and the kinetic energy disappears. In the actual fluid, friction is never absent, and is continually generating heat at the expense of the kinetic energy, and the temperature *even in the narrows* never falls as low as it otherwise would. There may be condensation into the liquid or even the solid phase in the narrows, but unless the liquid or solid can be trapped it will pass on with the current as a mist or sleet, gradually melting by the friction it experiences until in the wider part of the passage it will have a temperature greater or less than at start as indicated in the above considerations and shown in Fig. 2.

## PART I. -- LABORATORY METHODS OF LIQUEFACTION.

# On the lowest temperature yet obtained

BY

### Prof. Dr. H. KAMERLINGH ONNES.

Mr. President and Members of the Faraday Society and the British Cold Storage and Ice Association. It is with deep sorrow that I bring to remembrance here the great loss science has suffered by the death of my dear friend and colleague Prof. KUENEN, a not less heavy personal loss for myself. On account of his many-sided work in experimental and theoretical thermodynamics, Prof. KUENEN was highly interested in the present meeting. His most beautiful work, such as the discovery of retrograde condensation, lies in the domain of the equilibrium of the liquid and gaseous phases in which mixtures of gases separate. The part he would have taken in the discussion on industrial processes dealing with such mixtures would surely have been an important one. In the meantime he looked forward with great sympathy to my having the honour to address you. If it should prove that I could not read my paper personally he promised to do so. The day before his unexpected death I saw him bright and in full vigour and it is a deep sorrow now to remember that the happy conversation we had the last hour we spent together had its starting point in arrangements for the present discussion.

§ 1. **Introduction**. — When we approach the discussion of generation and utilisation of cold from the point of view of the application of liquefied gases in scientific laboratories and leave aside the study of the properties of matter at low temperatures, including the principles of thermometry in this domain, there are two points which come to the front. The first is to construct appliances which allow the making of measurements over all the range of temperatures that have become accessible. The second to descend to a lower temperature than hitherto has been done.

As to the first point the paper of Dr. Crommelin gives a full description of the equipment of the Leiden cryogenic laboratory. The paper is in your hands, so I have not to dwell on the details of this equipment. But I hope to be allowed to emphasize that the true characteristic of the Leiden laboratory is to be found in its having a staff and a body of helpers as could only be formed in the long run of time. By constant contact with precision research in different departments of experimental physics, as well as with the historical development of the means to carry over these researches to always lower ranges of temperature, this staff has become the possessor of traditions which allow of the application of all experience gained in mastering the successive cryogenic difficulties to the attack of new problems of most varied kinds. In this way the laboratory with its staff realises in fact what has become more and more an international desideratum of science. Science asks now in many departments for specialisation. An investigator working in a special line and desiring to do any of his experiments at low temperatures, say at those obtainable with liquid hydrogen, will evidently find great gain if in arranging his special apparatus for work at these temperatures he can dispose of the help of a well trained staff to make this arrangement as efficient as possible. And when he has to perform with this apparatus experiments which offer many difficulties in themselves, the help of this staff will allow him to concentrate all his attention on the experiments, the manipulation with hydrogen going on so to say as if with water.

The number of problems to be treated in this manner is increasing every day.

As I decided some 40 years ago to undertake work at low temperatures, of course I had the conviction that it would give results of value for our understanding of the properties of matter. But the extension and importance which the work in this direction has attained, has widely surpassed any anticipation of mine. During the time that moderate quantities of liquid air had become available for the experiments which first occupied my mind, the necessity of some time making measurements with liquid hydrogen made itself felt. Before hydrogen was liquefied, helium was discovered, which substance afterwards proved to extend enormously the domain opened by hydrogen. And again, before helium was liquefied the discovery of PLANCK's quantum lent a totally new aspect to low temperature work. After the liquefaction of helium superconductivity added an entirely unexpected field of research. So there is an ever increasing number of problems requiring work such as can be done in the Leiden laboratory. While on the one hand I shall shortly have the great satisfaction to be able to welcome the liquefying of helium in newly started cryogenic laboratories, on the other hand the international interest of the Leiden laboratory continuing its historical line of research becomes the more prominent.

There is one problem in this line which, as I said before, comes naturally to the front in the discussion of to-day. It is the extension to lower temperatures of the range in which researches can be carried out. And so I beg to be allowed to give a preliminary account of experiments leading to the realisation of the lowest temperature yet attained.

§ 2. **First experiments.** As soon as the efforts to liquefy helium had succeeded, it was of course investigated whether it could be solidified also. This was even tried on the same day on which helium had for the first time been seen as a liquid. The method used was that of evaporation under reduced pressure. Fig. 1 shows diagrammatically the apparatus in which for the first time liquid helium has been seen and the circulation apparatus that served to obtain it. After having been preliminarily cooled in an appropriate way the compressed helium passes through the spiral in the refrigerator in which it is cooled down to the temperature of the hydrogen evaporating at the air pump. Having been reduced to this extremely low temperature it enters the regenerator-spiral, the end of which is provided with a nozzle. Here it expands: part of it liquefies by the LINDE-process and the vapour returns between the coils of the regenerator-spiral, the escaping helium vapour being received in a gasholder and being compressed again by the pumps. The liquid helium collects at the bottom of the vacuum-glass of the liquefier, where its accumulation can be seen: the bottom part of the liquefier glass was unsilvered; the surrounding vacuum glasses, the first one containing liquid hydrogen, the second one liquid air, were also transparent. The glass with liquid air was protected against condensation of moisture from the air by a glass in which alcohol, kept at atmospheric temperature, circulated. At the beginning of the experiment that was intended to produce refrigeration by evaporation of the liquid itself, the nozzle was closed and the pumps were put out of action. The vapour emanating from the helium at the bottom part of the glass of the liquefier passed under atmospheric pressure to the gasholder. The helium was seen boiling quietly.

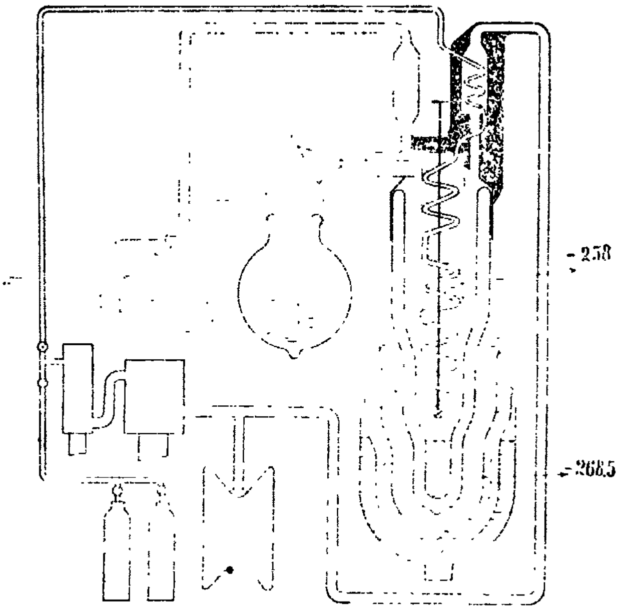

Fig. 1.

In order to follow the evaporation of helium at reduced pressure, it was only necessary to close the connection to the gasholder and to put into action the compressors now acting as vacuum pumps. The capacity of the pumps appeared to be great enough to remove the vapour so quickly that the temperature decreased considerably and, when their action was supported by a powerful vacuum pump, it was found that the pressure could decrease even to one centimetre, the helium still not ceasing to be a liquid.

At that time it was not possible to go further, as only an extemporized connection to the said powerful vacuum pump could be established. In 1909 the experiment was repeated after proper preparation to this end; the pump mentioned, a BURKHARDT pump with a capacity of 360 M$^3$. per hour, could develop its full power. Then it appeared that, even when the pressure decreased to two mms., the helium did not become solid. Though, at this low temperature, the liquid lost its peculiarity of having its surface standing sharply defined, like the edge of a knife, against the wall and now showed the ordinary properties of capillarity, yet its striking mobility remained.

With regard to the obtaining of solid helium, this result was disappointing. However, it appeared from this result that the region of temperatures in which the properties of substances could be investigated by means of baths of liquid helium extended farther than might have been hoped for by analogy with the other gases of low critical temperature, and so far the result was gratifying. For it is very difficult to obtain by means of some definite substance constant and homogeneous temperatures below the melting point of that substance. With helium the difficulties would be so great that the temperature of solidification might be considered a limit, below which it could not be usefully employed. Therefore in absence of a more volatile substance a limit would here have been put to science. Each time, when with further lowering of the vapour pressure it is found that the helium remains liquid, this failure with regard to the solidification of helium means a gain: a new region of temperature, which on account of its extreme situation is especially important, has proved to be accessible to us.

§ 3. **Improvements in the helium-cryostat and cycle** [1]. — Happily it has been possible to obtain a considerably lower temperature than has been mentioned above and we have arrived near the point, at which the low density of the vapours brings in a new limit, below which we cannot descend. To day I will deal with the experiments by which this lowering of the known limit of the liquid condition of helium has been obtained. This advance, however, has gone on gradually hand in hand with the regular developments of the laboratory and the last steps have only been possible after considerable improvement in various directions of the appliances for research in the region of helium temperatures. An important improvement was obtained when we succeeded in transferring the liquid helium from the apparatus in which it had been liquefied to a cryostat, in which like other liquefied gases it can serve as a bath for definite temperatures in the ordinary way. The cryostat *C* is still closely connected to the liquefier *L* (comp. fig. 2) but the room in the cryostat that is available for experiments is now no longer blocked at the top by the regenerator-spiral as in the first apparatus. The necessary appliances can be brought freely from the top *o* into the cryostat (comp. fig. 4*b*), whilst the bath surrounding the apparatus may be obtained by syphoning the helium from the liquefier into the cryostat. Such cryostats have been used already in several researches on the properties of substances at very low temperatures, especially in the domain of electricity and magnetism. Fig. 3 [2] shows the apparatus together with a diagram of the improved helium circulation, in which such a cryostat has been inserted. The helium, that liquefies on leaving the nozzle *k* of the regenerator-spiral, collects in the bottom part of the liquefier vacuum glass as in the first liquefaction experiments. This glass, however, is not closed at the bottom but ends in a double walled silvered syphon tube *s* (fig. 2), provided with a valve *r*.

---

[1] I gratefully acknowledge here a considerable augmentation of the stock of helium by the splendid gifts of the American Navy, 30 M$^3$., and of Prof. Mc Lennan, 6 M$^3$.

[2] Partly schematical, partly with the single objects to scale.

When this valve is kept tight, a supply of liquid helium can be collected in the liquefier glass. By opening the valve (comp. $v_0$, fig. 2 and fig. 5) liquid helium can pass to the actual cryostat. This cryostat itself consists of an unsilvered vacuum glass, in which the liquid helium is collected. This glass is surrounded by a second

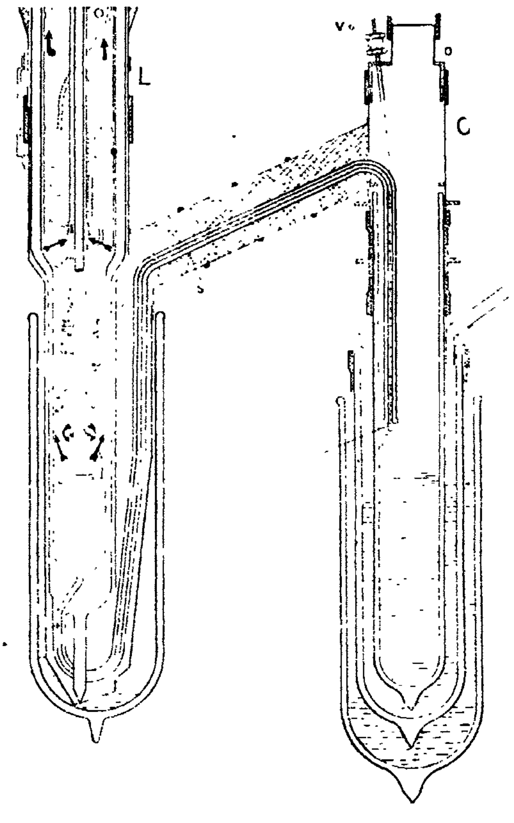

Fig. 2.

vacuum glass. In silvering it two vertical slits (comp. fig. 5, $p$) at opposite sides were been left clear to render visible what happens in the helium glass. The second vacuum glass is surrounded by a third one, silvered in the same way and containing liquid air. The vapours arising from the cryostat and those coming from the liquefier are received in the pumps $P_1$, $P$ (fig. 3) used for the following purpose; when the circulation is in action these vapours are driven back by the pumps to the liquefier, there to renew the supply of liquid helium. With the arrangement set up the process of liquefying helium may be continued, whilst the actual experiments are performed with the aid of the helium bath in the cryostat. As soon as too much helium has evaporated from the cryostat, the supply in the liquefier may be used to provide again the desired quantity.

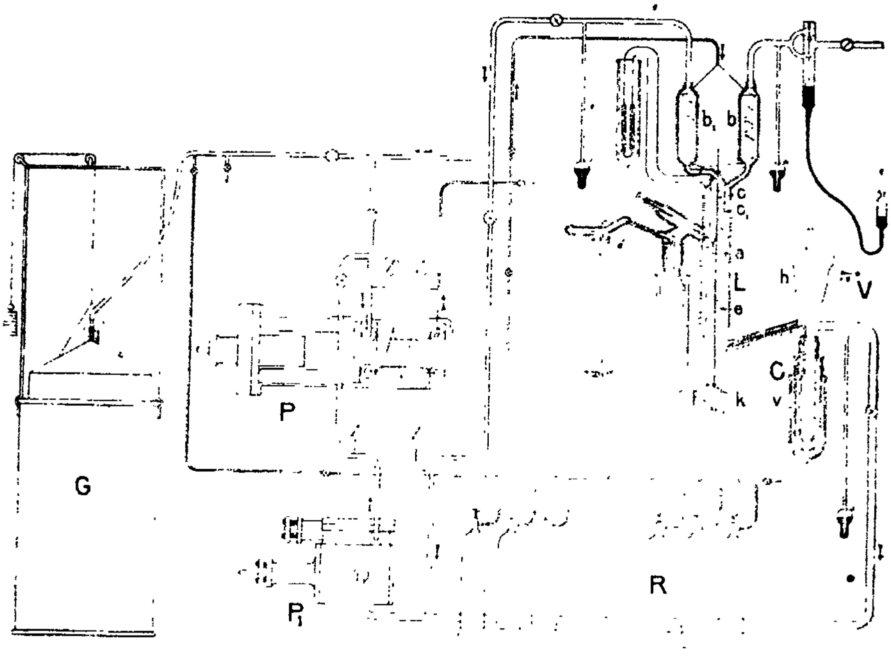

Fig. 3.

The improvement in dealing with liquid helium obtained by the separation of cryostat and liquefier, was accompanied by an improvement of the liquefier itself that led to a more rapid preparation of liquid helium and at the same time a more economical use of liquid hydrogen. The main part of the modification consists of a more efficient use of the available cold.

The helium, after being compressed to 30 atmospheres is divided (fig. 3) between two spirals $b$ and $b_1$ that unite again, bring the helium through a tube containing charcoal cooled in liquid air and are again divided into $c$ and $c_1$. $b$ and $c$ are cooled by cold hydrogen vapour arising from the liquid hydrogen in the refrigerator, $b'$ and $c'$ by cold helium vapour arising from the liquefier glass. Both spirals are much longer than in the first liquefier; they unite to form the spiral $a$ and pass, just as with the first liquefier, after cooling by hydrogen vapour surrounding $a$ and by liquid hydrogen surrounding $e$, into the regenerator-spiral $f$, which is provided with a nozzle $k$ [1]).

Besides obtaining in this way by better regeneration larger efficiency of the liquefactor, the capacity of the circulation has been increased by insertion of larger compressors $P$, $P_1$, which at the same time can act as vacuum pumps.

So in the new cryostats one had for hours at one's disposal a bath of say 500 cm$^3$. of liquid helium evaporating at a pressure of 3 mms. It was possible to perform extended experiments at temperatures whose attainment could hardly have been demonstrated in the early experiments with liquid helium. Such a cryostat with a bath of already extremely low temperature has been used with much advantage in the experiments on cooling helium still further by its own evaporation. The vaporisation apparatus (fig. 4), in which helium has been reduced to the lowest temperature that has been attained, consists mainly of a small double-walled vacuum flask $a$ (fig. 4$a$), containing the helium when it is cooled as much as possible, and of a wide outlet tube $b$ for the gas formed by the vaporisation. The vaporisation flask is immersed (fig. 4$b$) in the intensely cooled helium bath of the cryostat $C$; the gas escaping from the outlet $b$ leaves the cryostat through the lid $h$ which is connected to powerful vacuum pumps $V$ (fig. 5). It is evident, that those pumps not only must cause a high vacuum, but at the same time must have an extremely high capacity at the pressure of this vacuum, since the gas formed by the vaporisation will occupy a large volume at atmospheric temperature and at the low vaporisation pressure.

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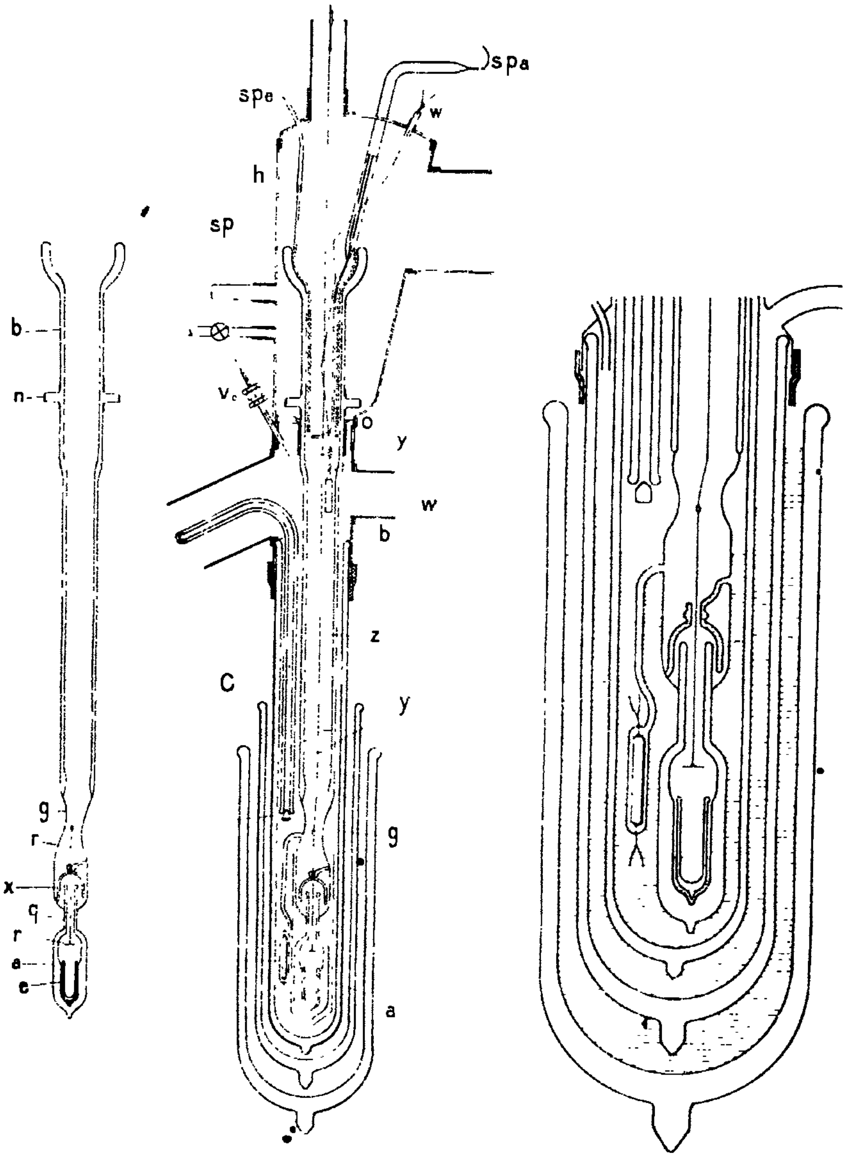
[1]) For further particulars see Leiden Comm. N°. 158 and Suppl. N°. 45.



*a* *b* *c*

Fig. 1.

Similarly it is seen at once, that the aim can be attained only if the cryostat affords opportunity to these large volumes of gas to escape by a wide outlet, as indeed it did in the apparatus used. If the tubes in which the gas moves are not very wide or are not at very low temperatures, the movement of the gas at the low pressures under consideration requires differences of pressure of the same order as that at which the gas is pumped away. These differences of pressure might form a considerable part of the pressure at which the helium evaporates.

§ 4. **Temporary set-back.** - These two considerations show already that great demands must be made on the appliances to be used for the experiments and especially on the capacity of the vacuum pumps, if descent to a very low pressure is aimed at. Now in 1910 an experiment had been performed in this direction on the same principle as has been followed now, but with insufficient appliances. Notwithstanding that the cryostat was deficiently conceived, by a fortunate accident a lower limit for the vapour pressure was reached than that obtained in 1909. Though this result could not be obtained again on repetition of the experiment with apparatus arranged in the same way as when the experiment succeeded, yet there was left no doubt that the vapour pressure could descend far below 2,2 mms. without solidification of the helium and that even at a vapour pressure of 0,2 mm. it would probably not solidify. This meant, however, that in order to ensure a quite certain progress, much higher demands had to be made on the experiments than when one stood only at 2,2 mms. as the lowest limit. Thus many years elapsed before one could think of lowering the limit below that accidentally found as 0,2 mm. and this problem had to be set aside and the treatment of various problems, more important for the moment and more in accordance with the gradual development of the appliances was first proceeded with; e. g. those concerning the superconductivity and the threshold value of the magnetic field by which ordinary resistance is generated in superconductors. The lowest temperature obtained remained that which corresponds to 0,2 mm. vapour-pressure. I had estimated this temperature at 1°,15 K. Taking into account the uncertainty of this estimation it would have been better to have said that *in descending one had approached to nearly* 1° K. As the state of the helium work progressed it became more and more necessary that a limit for the vapour-pressure more in accordance with its new feature than 0,2 mm. had to be given and especially it had to be established whether it would be possible to penetrate below 1° K. At last however in 1919, this problem could be attacked, when the difficulties of the years of war and of crisis had been overcome.

§ 5. **New attack.** — For the removal of the helium from the evaporation apparatus a large BURCKHARDT vacuum pump $V_{B_1}$ of 360 $M^3$. per hour capacity could then be used, coupled in series with one of 18 $M^3$. capacity $V_{B_2}$ and a SIEMENS pump $V$, of 2 $M^3$. capacity. The arrangement and treatment of the large high-vacuum pump $V_{B_1}$ were such, that there was no possibility of gas being given off from the lubricating oil into the vacuum. At the beginning the valves, which previously had been kept shut by means of *springs* until the gas by its own overpressure flowed from the pressure side of the cylinder into the outlet, were *now* opened and shut by a *mechanical arrangement* at the correct moment for the equalising of the pressure in both spaces. Later on the valves on the pressure side were taken away and the latter connected simply to the suction side of the auxiliary pump. With this pumping arrangement which had a limiting suction pressure of 0,04 mm. (in the best case 0,025 mm.) and with an evaporation glass which, though not so good as but in the main set up like that which served for the experiments which I shall describe, a volume of 2,7 litres of gas per hour (measured at N. T. P.) could be removed and the pressure of suction at the *top* of the cryostat reduced to 0,1 mm. It was concluded that the *vaporisation pressure* was again smaller than had been obtained in 1910, perhaps it may be estimated to have been reduced to 0,15 mm. When the pressure had fallen to this value, there occurred no further change in the evaporation, equilibrium between the heat received and the cooling by evaporation being attained.

The helium again did not solidify and the limit for the pressure had again been somewhat lowered, which again led to higher demands on later experiments.

§ 6. **Battery of condensation vacuum pumps.** -- Real progress could be made only by executing a long cherished plan, namely: the construction of a vacuum pump-complex of very large capacity with extremely low suction pressure. This was intended to consist of a large number of LANGMUIR condensation pumps connected in parallel. In 1920 the first step was made in the realisation of this plan and since then the battery

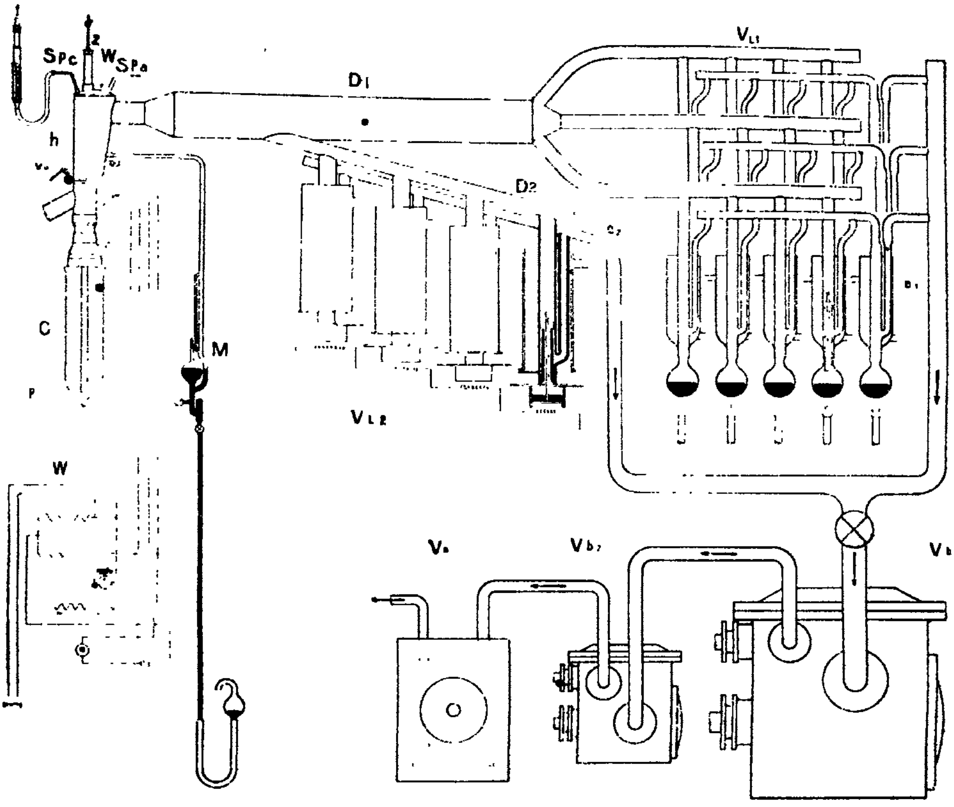


Fig. 5.

of pumps has been regularly enlarged[1]. In the experiments now described the battery had already grown (fig. 5) into

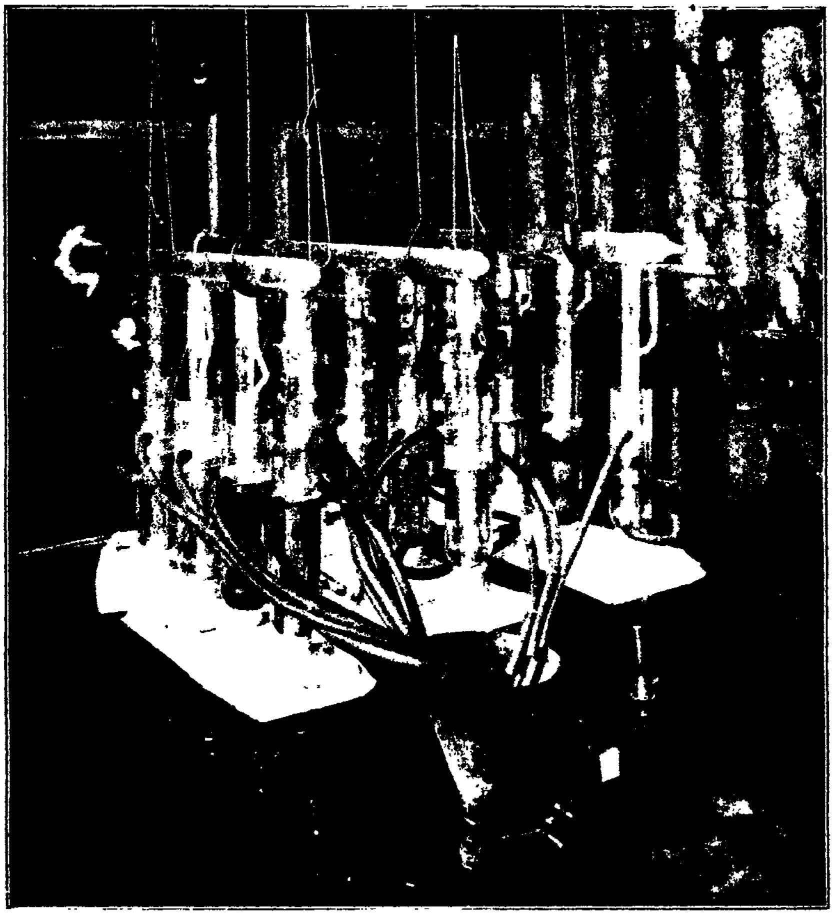


Fig. 6.

one of 12 glass ($V_1$) and 6 iron ($V_2$) LANGMUIR pumps, connected

[1] My best thanks are due to PHILIPS' Incandescent Lamp Works, Eindhoven, for presenting us, at the beginning of our attempts, with a number of these pumps.

in parallel into one single complex. The BURCKHARDT pumps connected as before in series served as the auxiliary pump. This is shown diagrammatically in fig. 5[1]).

The battery of twelve glass pumps (see fig. 6) consists of three series of four pumps, each series having (as later appeared superfluous) a LANGMUIR pump as auxiliary (fig. 5) before being connected to the actual auxiliary consisting of the complex of BURCKHARDT pumps. In this battery the mercury of the condensation pumps is heated by means of gas. Since flames are not permissible in such a room as the department for helium experiments, the battery is built into a small separate room in the department. The room containing the battery is ventilated with outside air by means of a fan, which maintains a blast of air through the nicks in the walls into the helium department [2]).

All connections to be found on the glass pumps were made by sealing together. The different series were cemented to the copper suction-tubes which united in a main $D_1$ of twelve cms diameter. As far as the copper tubes were not soldered to each other, they were cemented together just as the main is to the cap of the evaporation apparatus. The only connection by rubber was that of the tubes coming from the auxiliary LANGMUIR pumps to the suction tube of the Burckhardt $V_{b1}$. Further, all the copper used is varnished.

In general the iron pumps are not so suitable for the highest vacuum as the glass ones, but they are quite good enough to procure the high vacua with which we are concerned here. They are heated electrically and attention must be paid continually in order that one of the cemented connections does not give way. But I will not further dwell on these details, nor on the adversities and disappointments which necessarily accompanied the experiments which I am describing now, before they were concluded satisfactorily [3]).

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[1]) Partly schematical, partly with the single objects to scale. One should take into account the historical development.

[2]) In case of emergency all flames can be put out at once.

[3]) We must point out that if one of the pumps suddenly burst, a large quantity of air whould have to be received by the BURCKHARDT-pump. Besides

By the aid of the battery with which I am dealing now, on a suction-pressure of 0,005 mm. at the evaporation apparatus, a capacity of one litre (at N. T. P.) of removed gas per hour was finally obtained, corresponding with an evaporated quantity of 1,25 cm³. per hour of liquid helium at 2° K.

§ 7. **Minimising the heat conveyed to the evaporating helium.** — The very large capacity of the pumping arrangement may be utilised the better, the more the helium which has to be vaporised is protected against conveyance of heat and the more the frictional resistances between the evaporating helium surface and the pumps are diminished. Both requirements are, however, very difficult to combine in the construction of the evaporation apparatus: a wider outlet tube will diminish the frictional resistance, but at the same time it will give rise to a larger heat conveyance through the glass walls and especially by conduction in the column of gaseous helium in the tube. Both requirements have been satisfied as much as possible in the construction of the evaporation apparatus shown in fig. 4, which was used in the last experiments in 1920 and 1921. (For the meaning of some details of the construction see also §§ 9 and 10). Besides the small evaporation flask *a* with double-walled evacuated interspace and the similarly double-walled outlet tube *b*, the interspace of which can be evacuated through a tap [1]), we notice a single-walled part *g*. Advantage is taken of the latter to introduce, by means of an artifice, liquid helium into the evaporation-flask. To bring this about, helium is introduced into the helium space connected with the high-vacuum pumps, i. e. the evaporation apparatus, the connecting tube to the pumps and the pumps themselves, the battery of condensation pumps and the auxiliary pumps being out of action. The pressure is thus allowed to rise above the vapour pressure occurring in the bath of the cryostat. Inside, the liquid helium then flows down along the walls and so fills the bottom part of the apparatus. By again putting into

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safeties to the Burckhardt itself a shutting-slide has been placed in the suction-tube. This slide could be shut on the first signal.

[1]) Any small lowerings of the vacuum consequent on the presence of soldered metal can be remedied by these means whenever necessary.

action the auxiliary pumps evaporation under decreasing pressure is brought about until only the required quantity of liquid helium is present in the evaporation glass, in which, protected against heat absorption, it cools further until, to go lower, the high-vacuum pumps have to be put into action and the actual experiment can be commenced. The pressure under which suction occurs at the cap of the evaporation apparatus is measured with a McLeod manometer *M*, fig. 5. Special care has been taken to prevent heat penetrating by conduction or by radiation into the helium in the evaporation flask. It is necessary to pay attention also to the radiation given out by parts of the apparatus remaining at ordinary temperatures, e. g. that coming from the cap above the outlet tube through which the evaporised helium is led away. The order of magnitude of this radiation may be estimated by comparison with the total black radiation from a plane surface ($4{,}8.\ 10^{-9}.\ T^4$ gram-calories per hour and per cm$^2$.). Substituting the value of the ordinary temperature in this expression one arrives at 30 gr. cal., which, on account of the small heat of vaporisation of helium, about 6 cal., suffices to vaporise a quantity of liquid which occupies some 30 litres at N. T. P. when in the gaseous state. The pump-complex is, however, calculated to remove at the pressures under consideration only a quantity of gas corresponding to one litre at N. T. P. per hour. The radiation towards the evaporation flask should be received as much as possible by opaque metallic screens which are cooled down to low temperatures, preferably to the temperature of the helium bath in the cryostat. The radiation from screens cooled to this degree, on account of its dependency on the fourth power of the temperature, is so small as to be negligible. Protection against the radiation falling sideways on the walls of the evaporation flask may be especially easily realised: the entire lower part of the evaporation glass is surrounded by a metal bowl, the upper side of which extends beyond the surface of the liquid helium in the cryostat. In this bowl two slits are left open in order to render the evaporation flask visible through the unsilvered strips of the vacuum glasses. As a rule the slits are kept shut by means of two screens, which may be rotated around the bowl. They are removed only when the level of the liquid must be observed;

for illumination, use is made of a metal filament lamp, placed behind an alum solution. In order to shut off heat conveyance from above by radiation into the evaporation glass an arrangement has been constructed, by which the whole — made by Mr. KESSELRING, chief of the glassblower department — became a masterpiece of the glassblower's art. Above the evaporation flask *a* there is sealed into the glass a double-walled cap *x*, the interspace of which is connected to the outside of the vacuum tube. The helium in the cryostat flows through the annular space of the cap, the upper side of which is blackened and the lower silvered. Radiation from above can only penetrate by reflection along the walls of this cap. The heat transference from above has been further minimised by narrowing down the single-walled middle part as much as the strength of the apparatus and the quantity of escaping vapour would allow. Further, screens *y* cooled by the ascending gas and by other means to which we will refer later, were so placed in the outlet, that they did not hinder the free escape of the vapour The inner walls of the outlet were blackened with a mixture of soot and celluloid solution in order to diminish the reflecting power. Finally, there serves to the same end the spiral *Sp* that has been introduced at the top, through which liquid hydrogen is forced and which removes part of the heat which otherwise would have been conducted below by the walls. In another respect also advantage has been taken of the glassblower's art in the construction of this evaporation glass. As we have seen, the outlet tube has also a double-walled upper part, silvered and evacuated between the double walls. The stresses which originate on account of the great difference of temperature between the inner and outer walls are taken by a metal case *u* soldered to the glass and serving as a spring. The heat transferred from above to the lower parts through the walls across the narrowing is taken up by the bath of the cryostat [1], the level of the liquid in the cryostat being always kept above the narrow portion *g*. In this way it is tried to ensure that the temperature of the helium gas above the evaporation flask is not appreciably higher than that of the bath.

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[1] The heat thus deviated to the bath has no perceptible influence on the rate of evaporation and hence on the time during which the experiment can be continued.

The neck of the evaporation flask in which the evaporation under very low pressure occurs was long and narrow, firstly to reduce the heat conduction through the glass as much as possible, the small radius allowing the inner wall to be made very thin and secondly to make the velocity, with which the vapour escapes, great enough to carry away the heat which otherwise would enter by conduction along the column of helium gas. In all this attention has been paid to the limit at which disadvantageous frictional resistances would make their appearance.

All the above mentioned precautions having been taken to protect the helium in the evaporation flask as much as possible against heat transference, the vaporisation appeared to have been reduced to 0.9 litres of normally measured gas. The suction-pressure produced by the high-vacuum pumps at the cap of the evaporation apparatus was shown to be 0.0055 mm. by the McLeod-gauge.

In the hope of reducing the quantity of glass which finally had to be cooled down by the evaporating helium, an especially thin-walled small vacuum glass *e* was placed at the bottom of the evaporation flask. It was thought that on continued pumping the liquid in the small glass would continue to evaporate after the liquid surrounding the glass had evaporated, so that the circumstances for cooling the helium would become more favourable, as less glass had to be cooled and less heat would be conveyed along the wall. It will be seen presently that peculiarities in the course of the evaporation brought it about that the liquid level inside and outside the small glass sank at the same rate. As regards further progress in reaching lower temperatures, the bowl did not fulfil expectations.

§ 8. **Minimising the frictional resistance on the way from evaporating helium to pumps.** — I will now proceed to discuss the minimising of the frictional resistance of the vaporised helium in the evaporation apparatus on its way from the liquid surface

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to the high-vacuum pumps and hence using the low-suction pressure of the pumps to the best advantage at the evaporating surface. The width of the outlet tube could be increased only as far as the size of the top of the cryostat *o* (comp. Fig. 4*b*) allowed. The opening in the latter could not be widened without rebuilding the whole cryostat[1]).

With the greatest width at present available for the outlet tube, the gas would, as a consequence of receiving heat in ascending, acquire so great a velocity, that a frictional resistance much to large for our experiments would occur, unless special means were taken to prevent this. For this purpose there has been placed in the top of the outlet tube a lining that can be cooled strongly by external means. This lining consists of the copper spiral *Sp* through which liquid hydrogen can be led. The spiral is connected to a Dewar flask of liquid hydrogen and the liquid is forced under a small overpressure through the former; the supply being regulated by a flow-meter showing the quantity of evaporised hydrogen. Not only does this lining, through being thus cooled, reduce considerably the heating of the vapour in its ascent through the outlet tube and contribute to the prevention of radiation by the cooling of the various screens, but it also takes up, as we have said, part of the heat penetrating from above along the glass walls of the evaporation glass. By means of a small resistance thermometer placed under the lowest turn of the coil it can be ascertained whether the arrangement is working properly; in the experiments that succeeded best the temperature underneath the spiral decreased to − 200° C. Then the loss of pressure due to frictional resistance, as we shall see, is reduced to only 0,01 mm.

§ 9. **Determination of pressure.** — In determining the pressure in the space immediately above the level of the evaporating helium use was made of a resistance manometer. Pressures such as those which occur above the surface of the evaporating helium are too small to be measured by means of a suitable mercury manometer except with a very rigid arrangement such as would be very troublesome in this case. From this point of view a resistance manometer is already preferable. The manometer tube further may have very small dimensions and the manometer can be calibrated very well for pressures between 5 and 20 bars. Whatever manometer is used, if the space of the manometer is at ordinary temperatures and is connected to the space at the lower temperature by a narrow tube, the pressure in the manometer space will not be equal to that which has to be measured. At the low pressure at which the helium evaporates, the mean free path of the gas molecules, except where the connecting tube is at a very low temperature, is probably many times greater than the diameter of the tube. Between the space at low and that at ordinary temperatures there occurs a pressure difference equal to the thermal molecular pressure. The hope [1]) that this difficulty inherent in measuring pressures at low temperatures could be avoided by the use of the resistance manometer, as it was here possible to keep the manometer tube itself at a low temperature, has happily been confirmed by a series of experiments carried out in collaboration with Mr. VAN GULIK. So the pressure below in the evaporation flask has been determined by means of a resistance manometer, the manometer tube of which was kept at a temperature but little above that of the evaporating helium by being immersed in the helium bath outside the evaporation flask. In fig. 4*b* and *c* is shown how the manometer tube is sealed to the lower part of the evaporation glass; in fig. 5 the arrangements *W* for the measuring of the resistance are shown diagrammatically. At first sight it seems doubtful whether the principle on which the resistance manometer is based, viz. the change of resistance of the manometer wire with temperature, can be applied at a temperature so low that the resistance of the wire has not only fallen to a very small value but also does not change with temperature, as is the case with a platinum wire at the temperature of liquid helium. But it appears that the resistance remaining at this temperature, viz. the additive resistance, is still sufficient (if a still serviceable small current flows through the wire) to heat the wire until the temperature is reached at which the resistance begins to increase distinctly and so the influence of the pressure on the loss of heat from the wire becomes observable through the difference of current necessary to maintain the same resistance. Though the measuring apparatus, if used in this way, becomes a means rather of indicating than of measuring the pressure, yet by calibration at known pressures the desired aim is attained. In this calibration the apparatus was filled with gaseous helium at rest and with its lower end immersed in the same way as in the experiments in the helium bath. The upper part protruding into the cap of the cryostat remained at ordinary temperatures. The tube *b* is not wide enough to render quite superfluous a correction for the thermal molecular pressure between the upper and lower parts. The accuracy of the values of the pressures, which will be given presently, will be increased therefore, when the uncertainty resulting from the fact that the correction has as yet only been *calculated*, will be removed by new *experiments*. I will not dwell, however, at present on this correction, which is only 0,003 mm. Also we neglect the difference which may still exist between the pressure in the manometer tube and that at the surface of the helium itself.

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[1]) The extensive work necessary for the construction of a further cryostat with a wider opening at the top is in hand.

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[1]) Cf. Leiden Comm. Suppl. No. 34*a*.

§ 10. **Stirring arrangement.** Lastly we have to mention the small stirrer *r* introduced into the evaporation flask *a*. With the arrangement of the evaporation glass shown in fig. 4 it consisted of a horizontal glass disk attached to a vertical glass rod. It can be moved up and down by means of a wire *z*, attached to a rod, which passes a glass tube in the cap; the tube is closed by means of a packing gland[1].

§ 11. **The final experiments.** - For the success of the experiment with the complicated arrangement which has been described

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[1] In an earlier experiment a spring was inserted between the wire and the rod. A diamond was suspended from the wire instead of the disk. If the helium had solidified and the diamond had encountered resistance, the spring would have been stretched in its movement up and down.

(and of which fig. 7 gives a view), it is necessary that numerous operations should be performed each in the time allotted to it and in regular order, the success of each of the operations themselves depending upon careful preparation.

A small amount of condensation on one of the glass walls through which the evaporation of the helium must be watched suffices to render observation impossible: on walls cooled in liquid hydrogen a gas rendered impure by traces of air gives condensation. On reflecting on what is required to keep the glass walls through which it is necessary to see, perfectly transparent for hours after liquid helium has been introduced for the first time into the cryostat, it will be understood that I am greatly indebted to Mr. FLIM, the chief of the technical department, for his devotion to the work. Thanks to him everything went according to plan.

Fig. 7.

Early in the morning the preparation of 24 litres of liquid hydrogen was commenced, the previous day having been spent, on the one hand, in evacuating the apparatus and further putting it in working order and, on the other hand, in preparing a sufficient quantity (more than 50 litres) of liquid air. Meanwhile the following preparations were carried out: the helium circulation was further put in order; the pump, which had to remove the hydrogen from the helium liquefier at reduced pressure, was started; the space reserved for the liquid air used in cooling the hydrogen was next filled and the liquid hydrogen space filled, after having been first cooled with dry cold hydrogen gas. At 12 o'clock the liquid helium could be syphoned over into the cryostat, after which we proceeded to cool this bath further by evaporation and refilling by means of the helium circulation. At 1 o'clock the condensation of the helium, into the evaporation apparatus could be commenced and the bottom part of the evaporation glass was filled up to somewhat above the double-walled cap mentioned earlier. At about 3 o'clock this helium had evaporated so far as to occupy only the lower part of the evaporation flask, the evaporation taking place first under the action of the auxiliary pump complex, later on under that of the combined high vacuum and auxiliary pumps, which serve for the removal of the helium from the evaporation apparatus. The evaporation was further observed alternately with the naked eye and with the telescope of a cathetometer, the screens around the evaporation flask being kept shut as long as possible. Neither by means of the stirrer nor with the naked eye or with the telescope could anything be observed that pointed to the solidification of the helium even at the lowest vapour pressure observed: the liquid retained its great mobility throughout.

§ 12. **Evaporation at different levels.** — Further, it was observed that contrary to the expectation that the layer outside the small glass would evaporate first and then the helium inside the glass, both liquid levels fell at the same rate, so that they remained in the same horizontal plane. If (comp. fig. 8) by means of the lid shaped stirrer *r* (fig. 4*a*) liquid was thrown from the inside to the outside, the outside level fell rapidly while that of the liquid inside rose until they were again in the same plane. If, by removing the screens and allowing the radiation from a lamp to fall on the evaporation flask, the outer layer was caused to evaporate, after turning the screens the outer layer was re-formed at the expense of the helium within the small glass, and increased until both levels were at the same height, after which both again fell at the same rate. The speed of readjustment by this distillation was striking. A correct judgement on this phenomenon will only become possible, when the determinations we have in view concerning the heat conductivity of glass, of helium vapour and of liquid helium have been carried out, whilst a knowledge of the latent heat of evaporation and of the specific heat of liquid helium and of glass and of the viscosity of gaseous helium is also desirable.

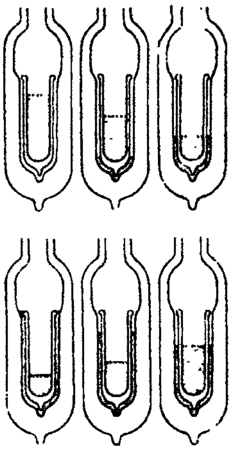

Fig. 8.

The property of a maximum density shown by helium has of course great influence on the observed evaporation. Observations in 1911 had brought this property to light, but it was not sufficiently established whether the density approached a limiting value or whether it decreased at still lower temperatures. That the latter is the case has been established by a repetition of the experiments undertaken in collaboration with Mr. **Boks** after the completion of the experiments with which we are dealing now. This confirmation holds only so far as the possibility of some peculiarity in the expansion of glass is excluded. On cooling the surface of helium below 2,2° K., the coldest layers of the liquid remain at the top. While in other cases in working with baths at reduced pressure care has been taken to stir vigorously, in this case stirring has been omitted, as this would have made a claim on the already small amount of available space at the top of the cryostat. The presence of a stirrer in the outside bath would probably have made the heat transference to the evaporation flask still smaller than it actually was. It was hoped that the means which have been applied would have reduced the heat transference to one half of what it seemed to be assuming that there is no special change in the latent heat of vaporisation.

**§ 13. Lowest limit of evaporation pressure.** — However this may be, when the level of the evaporating helium had fallen to the bottom of the narrowest part of the evaporation flask and to about half the height in the small glass, it appeared that the lowest vapour pressure was reached that could be obtained with this apparatus. Neglecting the small corrections mentioned above, the pressure at the surface was 0,012 to 0,014 mm., mean 0,013 mm. In the cap there was a vacuum of in the mean 0,005 mm. The pressure difference due to the friction of the rapidly escaping vapours of low density was in the mean 0,008 mm. This value agrees sufficiently well with the result of a special determination of the frictional pressure experienced by helium moving through the apparatus with the same velocity. In this control experiment the evaporation flask was substituted by a tube through which helium, cooled to liquid hydrogen temperature and of the same density as in the actual experiment, flowed with the same velocity. This control experiment gave 0.009 mm. The observed frictional pressure also agreed with an estimate based on the probable distribution of temperature along the column of ascending helium. In round numbers and allowing for the existing uncertainties we may say that the limit for the evaporation pressure has been brought below $^{1}/_{100}$ mm. and that we have progressed ten times as far as in the experiments of 1910 on which was based the estimate of the temperature mentioned as the lowest one then reached. In temperature difference as measured by KELVIN degrees this means, as we will see in § 14, only a very small range.

Returning to the question of the solidification of helium we come to the following conclusion: as there is provisionally no doubt that helium has a maximum density (see § 12) and as it is even not solidified at a temperature below the half of that of the maximum density we cannot escape the question whether helium will not *remain perhaps liquid even if it is cooled to the absolute zero.*

**§ 14. Determinations of temperature.** It still remains to consider the question of what temperature corresponds to the evaporation pressure found. For the latter pressure an experimentally established value can as we have done be given, apart from a few probably small corrections which demand further study; the same cannot be said of the temperature. In the determination of the extremely low temperatures, at which even the

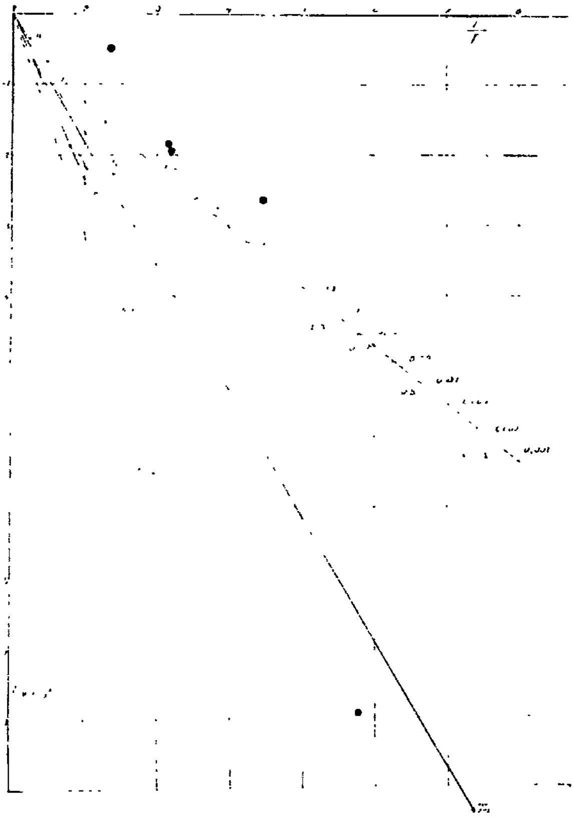

Fig. 9

helium gas thermometer can no longer be usefully employed, we enter a region the study of which has only commenced. Therefore we fall back on the law of corresponding states of VAN DER WAALS to guide us now in extrapolating the law connecting temperature and vapour pressure to lower temperatures than those for which it has been established experimentally. The latter has been done for the range in which it has been possible till now to use the helium gas thermometer. In this case the construction of the thermometer had to be adapted to the pressure, which introduced complications. In fact the pressure must be very low if the simple gas laws are to be applicable and even if only liquefaction is to be prevented. When the pressure becomes small, the correction for the thermal molecular pressure (the pressure difference between the thermometer reservoir at low and the manometer space at ordinary temperature) in this case also has to be applied. But notwithstanding these difficulties we succeeded in measuring vapour pressures of helium down to 1.5° K., in 1911 and 1913 with a thermometer with a mercury micromanometer and in 1917 with two thermometers with hot wire manometers. The results are plotted in the accompanying fig. 9, in which the abscissae are the reciprocals of the reduced temperatures and the ordinates the logarithms of the reduced pressures. The point is how to extrapolate the line which passes through the observed points. For this purpose the vapour pressure curves of ether, mercury, argon, neon and hydrogen are shown on the same graph ending in the triple-point of each substance. That for mercury has a still somewhat lower reduced temperature than has been reached with helium. All the curves agree in that the curvature is only very small, the greatest curvature with helium occurs at the higher temperatures. They deviate from each other in that the slope differs for the various substances. In the application of the law of corresponding states to normal substances account has to be taken of such systematic changes of the parameters of the laws for liquids: for substances with low critical point the slope of the line in the diagram decreases as the critical temperature decreases. In consideration of this it will be seen from the figure that helium satisfies this law in its generalised form; in particular the slope is compatible with that of *Ar*, *Ne* and *H*, the small curvature at higher reduced temperatures also falling into line. An extrapolation that can be accepted as a probable one, is that which is obtained by assuming the *tangent to the experimental curve at the point* where this curve ends, as its continuation. This has been drawn in the figure. It gives for the temperature corresponding to the limit of the evaporation pressure reached in 1910 the value 1°,15 K. and for that dealt with here, which is the lowest temperature yet attained, 0°,82 K.

Taking into account the uncertainty of the extrapolation it will be better to say that *the lowest temperature yet attained is some hundredths of a degree below 0.°9 K.*

§ 15. **Conclusion.** — The question put above, whether we could descend below 1° K., is answered positively by this result. In round numbers we have progressed $^1/_3$ of a degree and one may say that if we could have gone further only $^1/_6$ of a degree, we should have arrived at the limit obtainable in the ordinary way with helium. A better idea than given by these small numbers is obtained perhaps, when we express the lowering of temperature by the ratio in which we have decreased the absolute temperature. While the passing from ordinary temperature to that of helium evaporating at 0.2 m.m. means a lowering in the ratio 250 to 1 and from the melting point of hydrogen to the helium temperature mentioned, one of 13 to 1, the present lowering is only one of 1,4 to 1 and a further reduction of 1,2 to 1 would be nearly the limit of what could be done with liquid helium. If it is considered that our knowledge of atomic structure renders improbable that another substance could be discovered, or obtained in another way, more volatile than helium, then the limit indicated, from which we are separated by only such a small amount, would seem an absolute one set to us in the obtaining of yet lower temperatures.

We cannot accept such a limit otherwise than as a provisional one. There are even now definite problems which require to be treated in the domain beyond the seemingly impenetrable barrier. A simple example is the question whether a metal such as gold can be made super-conductive by cooling it more than we have been able to do. This kind of problem reminds us of the problem of the liquefying of the permanent gases. They withstood the efforts of the great experimenter whose glorious name is attached to your Society. Half a century later the liquefaction of hydrogen, the most incoërcible gas with which FARADAY had operated was the brilliant achievement of the latest of his successors in office at the Royal Institution: Sir JAMES DEWAR. We may feel sure that the difficulty which has now arisen in our way will be overcome also and that the first thing needed is long and patient investigation of the properties of matter at the lowest temperature we can reach.

# Apparatus and methods in the Leiden Cryogenic Laboratory

BY

## Dr. C. A. CROMMELIN.

§ 1. **Introduction.** The following article is arranged so that it gives a consistent description of the apparatus and methods used in the Leiden cryogenic laboratory; its purpose is to make it easy to find the exact places in the numerous communications in which the different appliances are treated. We have limited ourselves to a general outline; for the details, the original papers, to which the references refer, must be consulted [1].

The purpose of the Leiden cryogenic laboratory is and has always been to be able to produce *any* temperature below zero degrees, in order to be able to make accurate physical measurements at those temperatures. And the claim is, for accurate measurements at least, a constancy of 0°.01 during several hours. The best way to fulfill this claim is to make use of liquefied gases boiling, well stirred, under different pressures and keeping these pressures exactly constant. In Leiden only pressures of one atmosphere and lower (often as low as a few m.m., and in the case of helium a few tenths of a m.m.) are used, as the construction of cryostats for considerably higher pressures than one atmosphere is difficult and may even present danger. The region of temperatures covered by each substance is therefore the region between its boiling point and its triple point. In the following table is given a list of the substances used in Leiden, with the best values of their boiling and triple points; I have also added the triple point pressures, the critical temperatures and the critical pressures. For the better understanding of the following pages it will be useful to have all these data collected in a table.

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[1] For a description in full detail of some apparatus, which have not yet been published hitherto, especially the new hydrogen and helium plants and the methyl chloride and ethylene boiling flasks, see Comm. N°. 158.

| SUBSTANCE. | Boiling point. | Triple point temperature. | Triple point pressure in c.m | Critical temperature. | Critical pressure in atm. |
|---|---|---|---|---|---|
| methyl chloride . | 24°.1 | − 103°.6 | — | + 143°.0 | 65.98 |
| nitrous oxide.... | — 89.8 | − 102.4 | | + 36.50 | 71.65 |
| ethylene........ | 103.72 | — 169 | — | + 9.50 | 50.65 |
| methane.... .. | 161.37 | − 183.15 | 7.0 | 82.85 | 45.60 |
| oxygen........ | − 182.95 | 218.4 | ± 0.2 | − 118.82 | 49.713 |
| nitrogen........ | — 195.78 | − 209.86 | 9.64 | 147.13 | 33.490 |
| neon........... | − 245.92 | − 248.67 | 32.35 | − 228.71 | 26.86 |
| hydrogen....... | − 252.76 | − 259.14 | 5.07 | — 239.91 | 12.80 |
| helium......... | − 268.83 | − 272 | 0.002 | 267.84 | 2.26 |

In examining this table, one sees that the ranges of temperatures from −24° down to −218° C., from −253° to —259° C. and finally from −269 to −272° C. are attainable by baths of liquified gases; and that there are gaps between −218° and −253° C., and between −259° and −269° C. In the first gap there is still neon (from −246° to −249° C.), but this substance covers unfortunately only a small range. At the end of this paper the construction of the cryostats will be discussed; their construction depends of course on whether there is a boiling liquid available or not.

Let us first consider the different methods used in liquefying the various gases.

§ 2. **The regenerative cycles for the cascade: methyl chloride, ethylene and oxygen**[1]. — The principle of the Pictet cascade of cycles is so well known, that it need not be explained here. The construction, however, of the Leiden regenerative cascade differs in many respects from the original arrangement of PICTET, as will be learned from the following description. The first two steps in the cascade of temperatures are made by methyl chloride and ethylene. The methyl chloride, liquid at ordinary temperature under the moderate vapour pressure of about 4 atmospheres (if pure, otherwise a little higher) is stored up in a reservoir. In starting the cycle, a certain quantity is allowed to flow into the so-called boiling flask, made of german silver and constructed in such a way that it can resist the external pressure of the atmosphere and may thus be evacuated. The liquid fills only a small part of this flask. The boiling flask ends at the top in a very wide copper tube (nearly all the tubing in the cryogenic laboratory is of copper), leading to a powerful, fast running vacuum pump (from the Burckhardt factory at Basels) with a displacement capacity of 360 $M^3$. an hour.

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[1] Comm. N°. 87. See also Comm. N°. 14 § 4—7.

The compression outlet of this pump in connected with the vacuum side of a vacuum and compression pump (of the original COLLADON type used by PICTET from the Société génevoise at Geneva); these two pumps are thus connected in series.

The outlet of this compressor is finally connected to the above mentioned reservoir of the liquid. When the cycle is working and both pumps are running at the proper speed, the state of things is as follows: the liquid in the boiling flask boils, under the action of the vacuum pump, at the greatly reduced pressure of 1 to 1.5 c.m. at a temperature of about —85° to — 90° C. From the vacuum pump it goes to the compressor, where it is compressed at 5 to 6 atmospheres (depending on its purity, the temperature of the room, and that of the cooling water of the pump), liquefied and finally returned to the reservoir; then it goes again to the boiling flask etc. The rate at which the methyl chloride is circulated is from 18 to 20 $M^3$. gas (under normal conditions) an hour. All the valves being regulated properly, a stationary state is established and we maintain, as long as we let the pumps run, a large bath at about — 90° C. This is the first cycle; for which, of course, must always be chosen a substance which is readily liquefied at ordinary temperature.

We are now able to undertake the second step in the cascade. As substance for the second cycle ethylene (recommended by Cailletet, because of the large distance between boiling point and triple point and the moderate vapour pressure) is used in Leiden. As to the construction of the cycle, we may be brief, for it is nearly the same as in the case of the first cycle, with two exceptions only. First that the ethylene, not being liquefiable at the temperature of the room, cannot be stored up in a small reservoir (as in the case of the methyl chloride). Therefore a large vessel of 600 liters capacity has been inserted in the cycle. This container can hold a great part of the ethylene in the gaseous state. Secondly there has been inserted a condensation spiral of considerable length and surface in the methyl chloride boiling flask in order to liquefy the ethylene. Further the cycle contains a Burckhardt vacuum pump and a compressor connected in series, exactly as in the case of the first cycle. When now both pumps are running at the proper speed, we have the following state of things. the ethylene is compressed (but not liquefied) by the compressor at a pressure of 5 to 6 atmospheres and flows at this pressure into the condensation spiral. This spiral enters the methyl chloride boiling flask at the top and emerges from it at the bottom, while the methyl chloride vapour flows of course in the opposite direction. Thus the ethylene is first cooled by the methyl chloride vapour, which is about to leave the boiling flask, afterwards by the colder vapour in the middle of the flask and only finally by the liquid methyl chloride itself.

The upper part of the boiling flask works as a regenerator of heat and therefore the cycle is called a *regenerative cycle*. To assure the proper and economic working of such a boiling flask with condensation spiral care is to be taken that the rate of flow of the methyl chloride vapour and the ethylene, the length, the surface and the heat conductivity of the spiral and the heat insulating capacity of the walls of the flask must be such that: 1°. the ethylene is totally condensed before reaching its outlet and 2°. the methyl chloride vapour is allowed to „give off all its cold'' (if I may express myself in this way) to the ethylene. If in the construction of the boiling flask these conditions are fulfilled, the ethylene is completely liquefied and the methyl chloride vapour leaves the boiling flask at about the temperature of the room, *so that no external sign of cold can be seen* on the copper tube which leads to the vacuum pump. All external signs of cold, snow and ice on tubes or apparatus, are strictly forbidden in a cryogenic laboratory; they always mean „waste of cold'', i. e. waste of the thing we wish to get hold of and they are, as such, evidences that the working is not so economical as it ought to be. It may perhaps be stated here that in the Leiden laboratory external signs of cold are almost never seen.

The further working of the ethylene cycle may now be described in a few words. After having been liquefied, the ethylene enters the ethylene boiling flask at the bottom and boils there under a pressure of about 2 c.m. at a temperature of about − 150° C. under the action of the vacuum pump. The construction and (as will be seen afterwards) also the working of this boiling flask is so much the same as that of the methyl chloride boiling flask, that it is not necessary to dwell any longer upon it here. After having past the pump, the ethylene is led to the compressor, compressed to 5 to 6 atmospheres, then liquefied etc. The rate of circulation is here too about 18 to 20 M³. an hour. By the cycle we maintain a bath at about − 150° C. This temperature is considerably below the critical point of oxygen; and this gas can now be readily liquefied in the third cycle. The main apparatus in this cycle is the Brotherhood compressor [1]), with a capacity of 20 M³. an hour. This pump is lubricated with a mixture of glycerine and water; lubrication with oil presents danger, for the mixture of oil vapour and oxygen is explosive. It compresses the oxygen in three steps to about 20 atmospheres. The compressed oxygen enters the condensation spiral, which is arranged in the ethylene boiling flask very much in the same way as the ethylene condensation spiral in the methyl chloride boiling flask. The oxygen is liquefied and leaves the boiling flask

[1]) For an older type of Brotherhood compressor see Comm. N°. 51 § 3.

at the bottom through a well insulated copper tube, which leads to the oxygen boiling flask. The oxygen boils there at atmospheric pressure, at a temperature of —183° C.

It is not necessary to lower the pressure in this case, as will be made clear afterwards. A vacuum pump thus is not necessary in this cycle and the construction of the boiling flask is consequently much simpler than that of the ethylene and methyl chloride flasks. The oxygen evaporates in a rubber bag, from which it is sucked by the Brotherhood pump, compressed etc.

§ 3. **The liquefaction of air**[1], **nitrous oxide**[2], **methane and nitrogen**[3]. **General remarks.** — The fourth operation is the liquefaction of air. The air is first freed from carbon dioxide by letting it pass through a solution of caustic soda, then compressed by a Brotherhood pump of exactly the same type as the oxygen pump to about 15 atmospheres, and finally liquefied in a condensation spiral, which is contained in the oxygen boiling flask. It is collected in a large cylindrical vacuum vessel, from which it is syphoned into the spherical vacuum vessels of 3 to 5 L., in which it is stored up. About 14 L. of liquid air an hour are prepared in this way

A few general remarks.

It is hardly necessary to say that this rather complicated plant of regenerative cycles arranged in cascade has not been built to liquefy air. It has been built to work cryostats with methyl chloride, ethylene, oxygen and some other gases for physical determinations at all the temperatures from —24° to —217° C. When the use of vacuum vessels became easy and reliable so that liquid air was the appropriate mean to store cold for liquefying and other purposes, the apparatus for the liquefaction of air was added to the three existing cycles and this could be done in a exceedingly simple way, as was shown above.

Although not less than 4 compressors and 2 big vacuum pumps are running when air is liquefied, the whole installation works very economically, requiring only 23 H. P., that is 1,64 H. P. per $\frac{L}{\text{hour}}$. The well known LINDE and CLAUDE installations, although a good deal simpler in construction, require about the same amount of power.

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[1] Comm. N°. 14, XIII; 51, § 4 and 5.

[2] Comm. N°. 83, IV.

[3] Comm. N°. 51, § 1 and 5.

But let us return to our subject. Besides the gases already mentioned some other gases are sometimes liquefied, as will be seen on looking at the table in the introduction. The liquefaction is readily effected by the cooling agents of the cycles described, generally in rather simple apparatus which will not be described here.

Nitrous oxide is used only when temperatures from — 90° to — 102° C. (between methyl chloride and ethylene) are especially wanted; it is the liquid, which takes the place of the solid carbon dioxide; for with a solid it is difficult to get a good constancy of temperature.

In the same way methane fits exactly in the rather considerable gap between ethylene and oxygen, viz. from — 161° to — 183° C. In this region methane is regularly used.

Finally nitrogen is used chiefly in magnetic experiments, where magnetically indifferent liquid is required.

It is still worth while to draw attention to the fact, that in the Leiden installation the main substances have their own compressor, condensation spiral, boiling flask etc., which are never used for another substance. First this is a safety measure. Mixtures of several of the substances used would be explosive, and, in using the pumps for different substances alternately, the formation of such dangerous mixtures could hardly ever be avoided on account of the solubility of the substances in the lubricating oil. The matter is so evident, that it need not be explained more in detail.

But even if no explosive mixtures would be formed, the use of one apparatus for only one substance is absolutely necessary to keep the plant always in working order. Continually evacuating the apparatus, and especially the pumps, would be an enormous waste of work and time and the productive capacity of the laboratory would be considerably smaller than it is now.

§ 4. **The hydrogen plant**[1]. — The cascade method of PICTET, which can be so well adapted to the physics of low temperatures, fails below − 217° C. The lowest temperature which can be obtained with oxygen, boiling under a pressure of a few millimeters, is − 217° C., but this temperature is of no avail for the liquefaction of the next gas, viz. hydrogen, for this gas has a critical temperature of about − 240° C. (the use of neon will be discussed later).

Another method, that of the LINDE process, making use of the JOULE-KELVIN effect, has to be applied. We will not dwell here upon the possibilities of other methods. In making use of the JOULE-KELVIN effect it has to be taken into account that at *ordinary temperatures*, the effect gives a slight heating for hydrogen and helium, so that hydrogen and helium have to be cooled below the inversion point before expanding.

I will give now a short description of the hydrogen installation, as it now stands[2].

The gaseous hydrogen is compressed up to 150 to 200 atm. by a set of four horizontal pumps obtained from the Burckhardt factory at Basels. They run quite slowly (100 revolutions per minute) and compress the gas to the required pressure in 5 stages. The first pump compresses 40 M$^3$. of gas an hour from 1 to 2 atm.; the second pump works in 2 steps, the first one from 2 to 6, the second one from 6 to 25 atm. The third and the fourth pump are connected in parallel and each operates on half of the gas. They both work in 2 steps also, the first step compressing from 25 to 50, the second one from 50 to 250 atm., but generally a final pressure of 150 to 200 atm. is used. Between the different steps the hydrogen is thoroughly cooled in spirals in cooling water.

The compressed gas now comes into the liquefier, of which fig. 1 gives a schematical representation. The gas comes in at A where the tube is divided in 2 parallel tubes. One portion of the gas goes through the spiral $B$ (spiral wound tubes are represented by zigzag lines), the other one through $B'$; these spirals are united again at $C$. The hydrogen continues its course through the spirals $D$, $E$ and $F$ and finally expands to atmospheric pressure through the expansion valve $K$ (handle $K'$). It is partly liquefied, the liquid is collected in the vacuum glass $G$ and is syphoned through the valves $S$ and $S'$ into the vacuum bulbs $H$ and $H'$. In these bulbs the hydrogen is transported to the different rooms of the laboratory.

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[1] Comm. N°. 94f, X (the old plant), N°. 158 (the new plant).

[2] The original liquefier, of which a description in full detail may be found in Comm. N°. 94f, X, § 2, is still preserved to be used, if necessary, as a reserve apparatus.

As one easily sees, the construction of the apparatus is such as to cool the compressed hydrogen flowing in the direction of the expansion valve as efficiently as possible by the cold vapour, flowing in the opposite direction, according to the regeneration principle.

This principle is, as we saw, also applied in the construction of the boiling flasks in the cycles. Moreover, cooling by means of liquid air is absolutely necessary in the case of hydrogen to bring it to the temperature where the JOULE-KELVIN effect gives cooling.

Liquid air is used as a refrigerating agent: it is poured through the valve $L$ into the vacuum glass $E$ and it evaporates there under a pressure of about 2 m.m. maintained by the action of a powerful vacuum pump (displacement capacity 360 $M^3$. an hour). In this way the liquefier is started. From the moment that the first small quantity of liquid is collected in $G$ — about half an hour after the beginning of the expansion - the cold vapour of the liquid hydrogen does its work in the process of regeneration. And when finally a stationary state is reached, the regeneration acts so well that no external signs of cold are seen. The figure shows clearly enough that the hydrogen is cooled in $E$ by the liquid air itself, in $D$ and $B$ by the vapour of the air, in $B'$, $C$ and $F$ by the vapour of the hydrogen. Especially interesting is the capacity of this liquefier to produce liquid: this is 13 L. of liquid an hour in continuous working, i. e. for as many consecutive hours as is wanted.

§ 5. **The purification of the hydrogen.** — It is hardly possible to operate a hydrogen liquefier with commercial hydrogen on

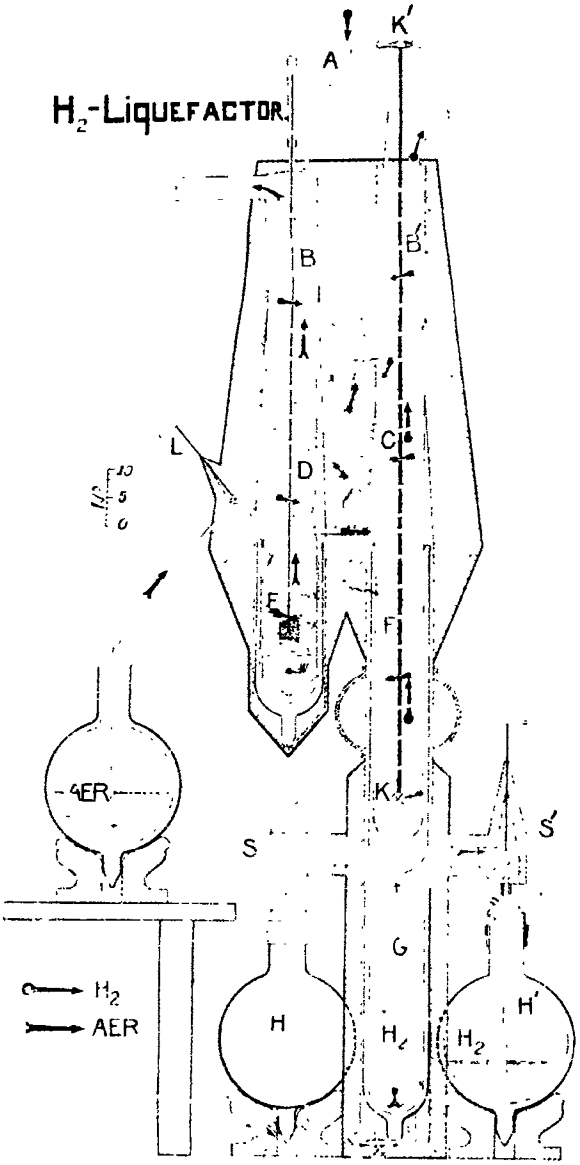

Fig. 1

account of the impurities contained in the latter. As these impurities very often amount to 2 or 3 %, they block the narrow spirals and the expansion valve some time after the starting of the apparatus. It is then impossible to work even for a couple of hours. Thoroughly purified hydrogen is absolutely necessary. When no liquid hydrogen is available, a separator [1], in which the compressed gas is cooled to the temperature of liquid air, may be used. But this apparatus does not deliver the hydrogen pure enough to avoid blocking: for solid nitrogen has even at − 217° C. (lowest temperature of liquid oxygen) a still rather considerable vapour pressure. Generally after the preparation of about 4 litres of liquid, the liquefier has to be stopped and heated before the work can be continued. The evaporating hydrogen, which is of course perfectly pure, is then carefully collected. After some time of working in this way, a sufficient quantity of pure gas will be stored up to keep the apparatus running for a longer time and to be able to make use of an improved separator [2] which is in constant use now. The impurities are removed in this apparatus by cooling the gaseous hydrogen down to the temperature of liquid hydrogen. The construction of this separator is extremely simple: a wide copper spiral is mounted in a silvered cylindrical vacuum vessel; liquid hydrogen is sprayed by small quantities underneath this spiral; it evaporates and cools the tube internally to about − 253° C., the temperature of boiling hydrogen, at which temperature the vapour pressure of nitrogen and oxygen are entirely negligible. The gaseous hydrogen flows through the vacuum glass, at the outside of the cold spiral: the impurities are deposited on the spiral and the hydrogen leaves the separator entirely pure, if its speed is regulated properly. Once having got a stock of pure hydrogen, compressed in cylinders, this stock must be considered as a first condition of working.

This separator is a small and handy apparatus, and delivers 5 M³. of perfectly pure hydrogen an hour. As soon as working with this separator was started, the difficulties with the impurities of the commercial hydrogen were quite overcome.

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[1] Comm. N°. 94*f*, XI.

[2] Comm. N°. 109*b*.

§ 6. **Safety devices.** - In describing the hydrogen plant I have been rather schematical and I have not dwelt upon many details and auxiliary apparatus although they are quite interesting from a technical point of view. They may be found in the original memoirs But I have to insist on the care that is bestowed on assuring safety in the cryogenic laboratory. Hydrogen being combustible there is especially danger of explosion by mixing with air. Every possibility of electric sparks, so easily obtained by the friction of solid particles in the cold gas, must be avoided with the utmost care. The same applies to methyl chloride and ethylene. Ethylene has the advantage over hydrogen that one can smell it, but it has about the same density as air so that it does not rise immediately to the ceiling like hydrogen. We had learned from our experience with methyl chloride and ethylene, which substances are used in large quantities and at rather high pressures how to work with hydrogen. In fact, protection is now a strong tradition which has established itself by long practice in the laboratory, so strong, that the scientific and the technical personnel take it as a matter of course that in every experiment safety is given the first consideration. Work has often been very seriously handicapped for this reason but every sacrifice has to be made in this direction without sparing in the least time or trouble. During some 35 years' working with large quantities of combustible gases a serious accident has never happened in Leiden and no bystander has ever been hurt.

§ 7. **The helium plant** [1]. The liquefier now in use has many advantages above the original one, which is kept to be used as reserve. It is built according to exactly the same principles as the hydrogen liquefier; i.e. preliminary cooling (here with liquid hydrogen) below the inversion point of the JOULE-KELVIN effect, expansion through an expansion valve; and in the stationary state cooling by helium vapour according to the regenerative principle.

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[1] Comm. N°. 108 (the old plant), N°. 158 (the new plant).

We reproduce a schematical drawing of this liquefier (fig. 2).

The gaseous helium compressed at about 30 atmospheres enters at *A* and is divided in 2 spirals *B* and *B'*. These spirals are united afterwards and then divided again in *C* and *C'*; *B* and *C* are cooled by cold hydrogen vapour, *B'* and *C'* by cold helium vapour. Now these spirals are finally united in the spiral *D*, cooled in the coldest hydrogen vapour and in *E* cooled in the liquid hydrogen itself. *F*, the last regeneration spiral ends in the expansion valve *K*. Here the helium is liquefied and runs through a vacuum tube into the cryostat, which is directly connected to the liquefier. We shall describe this cryostat afterwards.

As to the stock of helium, the first quantities were prepared from monazite sand. In later years Prof. ONNES received on several occasions presents of helium or of gases which contained more or less considerable quantities of helium, e. g. from Mr. GEORGES CLAUDE at Boulogne-sur-Seine and from the Welsbach Light Company at Gloucester N. Y. But during the war there was no longer any chance of such presents and at last the quantity available was hardly 300 litres so that the situation began to become critical and a new preparation was considered, if monazite sand could be obtained. Fortunately this trouble was spared. The American Navy in 1919 made Prof. ONNES a present of not less than 30 $M^3$ of helium prepared in Texas during the war for the filling of airships. And Prof. MC LENNAN of Toronto himself brought to Leiden in September 1921 a big cylinder, containing about 6 $M^3$. of helium, which had been prepared by him in Canada for the same purpose. The stock of helium is now so plentiful, that it will certainly last for a great number of years.

At the end of this sketch of the Leiden helium installation, I will once more emphasize the fact that the plant is built as a circulation apparatus more or less in the style of a cycle of the PICTET cascade. The gas circulates many times before the appearance of the first drop of liquid. If the gas could not be

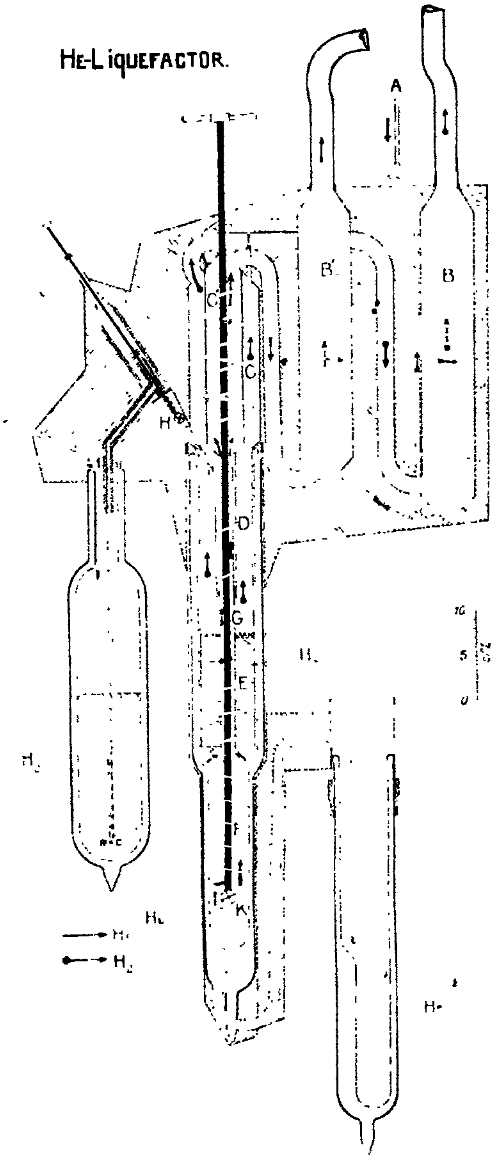

Fig. 2

compressed again after the first expansion and so forth (but had to be stored up e.g. in a gasometer) then a quantity of helium, twenty times as large as we now have, would be necessary, just to start the liquefier. This example makes it particularly clear that circulation is entirely indispensable in this kind of cryogenic work.

§ 8. **Liquid neon** [1]. By means of the cycles of methyl chloride, nitrous oxide, ethylene, methane, oxygen and hydrogen, the laboratory has available baths of liquids from −24°, down to − 259° C., with the exception of the region between 217° (oxygen, boiling under a pressure of a few millimetres) and 253° C. (hydrogen boiling under atmospheric pressure) and this region was for a long time unattainable for accurate measurements. The possibility of a bath of hydrogen boiling under the pressure of a few atmospheres has been considered, but the cryostat has not been constructed. With a bath of liquid neon (boiling point − 245°.92 C., triple point 248°.67 C.) a small range of temperature could be covered. The construction of such a bath has indeed been accomplished. Compressor, liquefier etc. were not necessary, for neon is solid at −253° C., and there was sufficient liquid hydrogen available to obtain the desired result with a very compact and simple apparatus. This apparatus is very much like the separator for the purification of the hydrogen. It consists of a long wide copper spiral in a cylindrical vacuum vessel. Liquid hydrogen is sprayed underneath this spiral, it evaporates and cools the spiral internally, if necessary down to 253° C. The neon flows through the vacuum glass at the outside of the spiral and condenses on it in solid or liquid state. At 253° C. neon is solid, but by proper regulation of the quantity of hydrogen, the spiral is brought to a somewhat higher temperature, so that the neon becomes liquid and drops off from the spiral. It finds its way through a vacuum tube at the bottom of the vacuum glass to the cryostat, a second vacuum glass immediately connected with the liquefier. In this way a bath of liquid neon was realised in a very simple way.

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[1] Comm. N°. 147c.

A small range of temperatures could be covered by this bath and in 1915 it has actually been used for the determination of some physical constants of liquid neon. It has some advantages above a bath of liquid or gaseous hydrogen especially in researches in which electric sparks occur; but the main disadvantage was the smallness of its range of temperatures. Therefore other methods were introduced, which could bring the whole range from 217° to 253° C. within the reach of accurate measurements. These methods will be discussed later on[1]).

§ 9. **The purification of the neon.** Working with a bath of liquid neon is only possible if a rather considerable quantity of neon is available. We mentioned already the present of Mr. GEORGES CLAUDE viz. a large quantity of gas, containing the most volatile distillation products of liquid air. This gas contained, besides helium, about 30% of neon. In this way the laboratory came in possession of a few hundred litres of neon. For a first purification, the gas was solidified by means of liquid hydrogen and the helium and hydrogen were pumped off; then the neon was heated up slowly and the evaporating gas chiefly consisting of neon was stored up separately; the less volatile impurities oxygen and nitrogen then remained solid in the tube. This operation was repeated several times. Finally it was passed over charcoal in liquid air according to the well-known method of Professor DEWAR. Accurate measurements showed afterwards that this purified neon was not so pure as we thought. Therefore a more refined and accurate method of purification was designed and applied by the author, with a view to determination of the critical point, vapour pressures and the rectilinear diameter of CAILLETET and MATHIAS. First the method described above was applied, but now in an apparatus entirely made of glass, without any rubber tubing; only the middle fraction was used. Finally the neon was allowed to flow very slowly through a wide glass spiral immersed in liquid hydrogen; the neon had to be kept below its vapour pressure at −253° C. (about 12 m.m.) in order to avoid solidification. Traces of less volatile impurities were deposited against the walls of the spiral. Finally it was fractionated once more. In this way a very pure product is obtained.

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[1] § 11 of this article.

§ 10. **The cryostats for liquids.** Hitherto, we have only spoken of the apparatus for the liquefaction and the purification of the different gases. To make accurate physical determinations however, we need special apparatus in which we may keep the temperature of the liquid constant and everywhere the same, and which may contain the substances of which we want to study the properties at low temperatures. These apparatus, the so-called cryostats, are at the present moment for us even more interesting perhaps than the liquefying apparatus. Formerly the state of things was different; then, the main problem was the liquefaction itself and collecting a few cubic centimeters of liquid oxygen or hydrogen was a success in itself. Now the methods of liquefying even the most difficult liquefiable gases are well developed and our attention is more fixed on the possibilities of determining accurately physical constants at low temperatures. The construction of cryostats with a constancy of 0.01 of a degree represents at the present moment a most interesting problem.

In Leiden many models have been in use in the past years. But as we are not giving a historical sketch of the development of the laboratory but only a (rather short) account of its present state, we confine ourselves to the description of the largest model for universal use with all liquid gases (except neon and helium), which is employed now [1]. Fig. 3, in which two cuts of the apparatus are given, may be understood without a long explanation. A few remarks will do. The large vacuum vessel V (internal diameter 12 c.m.) contains a german silver cylinder, in which the liquid (average 2½ litres) is poured. The glass is covered by a cap in which are openings for the apparatus, for the inlet of the liquid and for the outlet of the vapour (the latter leading

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[1] We will not dwell here upon the construction of cryostats for special purposes.

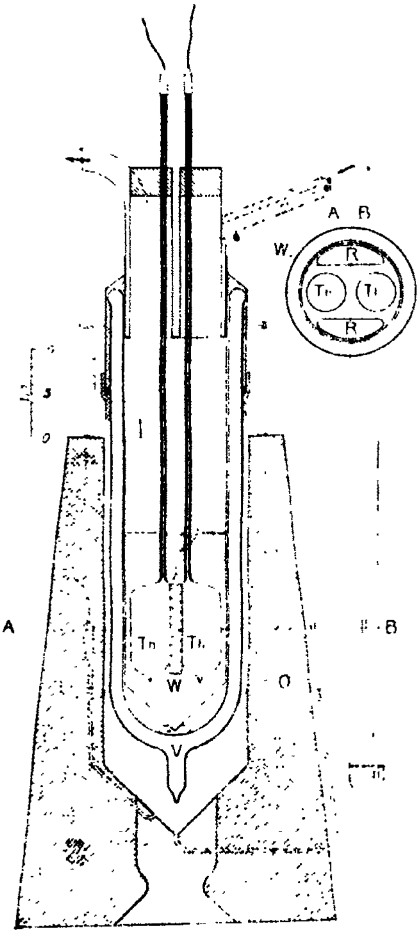

Fig. 3.

to a gasometer or to a vacuum pump). The vacuum vessel V' is enveloped by liquid air in order to diminish the rate of evaporation of the cryostat liquid and to improve constancy of the temperature. Generally, in the smaller types of cryostats[1] (which are built in exactly the same way as this largest one) the air is contained in a second, larger vacuum vessel. But as 12 c.m. is about the limit for cylindrical vacuum vessels (at least when they are made of ordinary „Thüringer" glass) the liquid air enveloping this cryostat is contained in a german silver cylinder, insulated by means of thick walls, filled up with cotton wool. The figure shows further (as an example of apparatus) the two reservoirs *Th* of a differential gas thermometer, two resistance thermometers *W* and two stirrers *R* (see also the horizontal cut). These stirrers work with valves and literally pump the liquid round. The sensitive oil manometer, by which very slight irregularities in the pressure are immediately seen, is not represented in the drawing.

The helium[2] and neon cryostats[3] are in principle very much the same as the cryostat now described only their arrangement is different. Most of the liquids in use are „transportable", that is to say, they are transported in vacuum bulbs from the liquefaction plants to the rooms where the cryostats are installed. With helium and neon this transportation is not, or at least not yet, possible on account of the costliness of the substances (little losses in transporting cannot be avoided) and, as to helium, on account of the volatility of the liquid helium. Therefore the helium and neon cryostats are connected immediately to their liquefiers in such a way that the liquid flows from the liquefier directly through a vacuum tube into the cryostat.

§ 11. **The hydrogen vapour cryostat**[4]. We have seen in the introduction, that there are two gaps in the range of temperatures which can not be attained by means of a boiling liquid viz. from — 217° to — 253° C. (except for a small part by liquid neon, this has been discussed already in § 8) and from — 259° to — 269° C. To attain the temperatures of the first gap, a hydrogen vapour cryostat is now in use in Leiden. Of this instrument, fig. 4 gives a cut in full detail. It is a rather complicated apparatus but it gives the required constancy of temperature (0°.01) very well during several hours; only the uniformity of temperature in the experimenting chamber is not yet exactly what it ought to be. The principle is, that the experimenting chamber *E* is kept at constant temperature by a current of cold hydrogen vapour. Before entering the chamber, the hydrogen is heated up to the required temperature by an electric heating wire in which the current is regulated by a very delicate automatic arrangement.

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[1] Comm. N°. 83, III and IV, 94c, 94d, 94f, XII.
[2] Comm. N°. 119, 123.
[3] Comm. N°. 147c.
[4] Comm. N°. 151a, 154c.

The vacuum vessel *V* is half filled with liquid hydrogen, the vessel *B* contains the experimental chamber *E*. Both vessels are connected by the vacuum tubes $b$ and $b_{11}$, and are enveloped by the big glasses $B_1$ and $V_1$, which contains liquid air. The gaseous hydrogen enters at $b$, at a pressure a little higher than atmospheric, is conducted to the bottom ($b_1$) of the vessel *V* and rises from there in bubbles to the surface of the liquid hydrogen. In this way we get a rather effective and adjustable evaporation of the liquid (average 80 litres an hour). The evaporating hydrogen follows the arrows in the figure and arrives at last at $b_2$ at a temperature only slightly above −253° C. in the heating chambers. There, it is heated to the required temperature and enters immediately the experimental chamber *E*. The heating chambers contain, besides the heating coils $W_1$, the helium thermometer $H_1$, connected by the steel capillary *C* to the mercury manometer, which regulates the heating current automatically by the contact at *A*. If the hydrogen is slightly to warm, then the current is broken and the heating stops; if it is too cold then the mercury rises and the current is switched in. I suppose that this short account will give a sufficient idea of the working of this apparatus.

Such a kind of cryostat is not yet available for the second gap, from −259° to −269° C.

From a theoretical point of view, the temperatures in question may be reached, either in a helium vapour cryostat of the same model as the hydrogen vapour cryostat, or (those below the critical temperature of helium) in a cryostat with helium

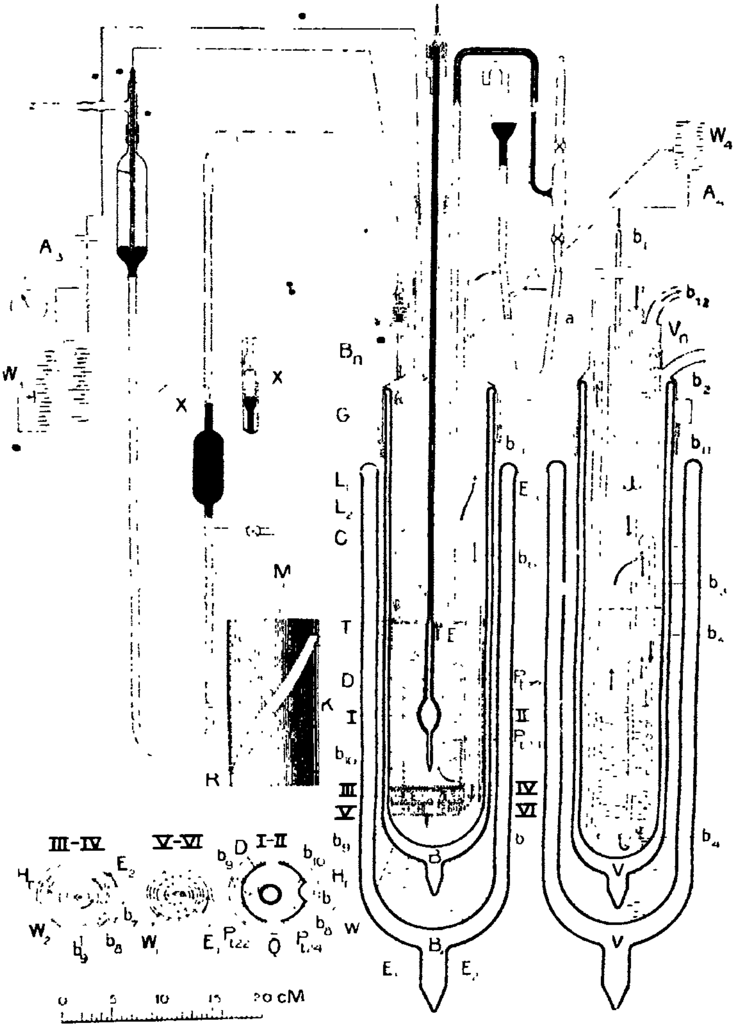
W₄
A₄
A₃
b₁
b₁₂
Vₙ
a
Bₙ
X
X
W₁
G
b₂
b₁₁
L₁
L₂
C
E
b₆
M
T
E
b₅
b₄
D
K
P₁
I
II
P₂
R
b₁₀
III
IV
V
VI
b₉
b
b₄
III-IV
V-VI
I-II
H₂
E₂
b₉
D
b₁₀
H₁
b₇
b₈
W₂
b₉
b₈
W₁
E₁
P₁₂₂
Q
P₁₄
W
B
V
B₁
V
E₁
E₂
0
5
10
15
20 cM

Fig. 4.

boiling under increased pressure. Both constructions have been considered but not yet carried out at the present date. A helium vapour cryostat of a construction different from that of the hydrogen vapour cryostat has been used recently for determinations concerning supraconductors. A description will be published before long[1].

[1] Leiden Comm. N°. 160*b*.

# ETHYL CHLORIDE ($C_2H_5Cl$).

### BY PROFESSOR C. F. JENKIN, C.B.E., M.A.

Ethyl chloride is a colourless liquid a little lighter than water; as its boiling point at atmospheric pressure is 12·5° C. it may be handled in open vessels without much loss and may be stored in glass bottles or cylinders of quite moderate strength.

It is an anaesthetic, but must be inhaled in considerable strength before it has appreciable effect.

It is very inflammable and considerable care must be exercised to avoid fires.

It is a very convenient material for refrigeration; the following data indicate its properties as a refrigerant:—

Latent heat at 0° C. = 93·7 cal. per gram, or C° lb. per lb.
Specific heat of liquid = ·348 at − 30° C. to ·413 at + 40° C.
,, ,, ,, gas = ·22 to ·28.
Specific volume of liquid { at − 30° is 1·035 c.c. per gram.
{ at + 30° is 1·139 ,, ,, ,,
,, ,, ,, gas (saturated) { at + 20° is 297 c.c. per gram.
{ at − 20° is 1305 ,, ,, ,,

The critical point is 190° C. and 54 atmospheres.

The vapour pressure curve is shown in the accompanying figure.

It does not attack metals, but for some reason not yet fully explained, the liquid does contaminate mercury, so that mercury manometers can only be used for pressures less than the vapour pressure corresponding to the room temperature—*i.e.* roughly for pressures less than atmospheric.

It attacks india-rubber, but vulcanised rubber tubing and corks can be used, though they leak a little. They swell considerably, but return to their original size when the ethyl chloride dries off. Pure rubber tape is softened almost to solution. Vulcanite swells moderately. It causes most woods to swell, but lignum vitæ can be used for valves, etc., when a non-conductor of heat is required. Bakelite is also useful as a non-conductor; it only swells very slightly.

Liquid ethyl chloride dissolves a small quantity of water, but can be dried by passing it through calcium chloride drying tubes. With water it forms very remarkable ice crystals; if a shallow glass of ethyl chloride is exposed to the air, it dries up and rapidly falls in temperature and ice crystals form round the edge, condensed from the atmospheric moisture. These crystals appear to be tubular and grow rapidly, the ethyl chloride soaking up inside them as in a sponge. Similar crystals form at the throttle valve in a refrigerating machine if there is any water dissolved in the ethyl chloride and quickly choke the valve. It is important, therefore, to keep the material dry in refrigerating plants.

Ethyl chloride is a convenient cooling material for use in laboratories; when sprayed on to any object the temperature is quickly reduced to − 20° C. or lower.

For mechanical refrigeration ethyl chloride is very suitable. The vapour compression cycle is the one used. The pressures corresponding to the ranges of temperature commonly required are very low, for example for a range of ± 20° C., the pressures are 19·4 and 3·5 lb. per sq. in. absolute; the compressor therefore works with a moderate vacuum on the suction side. The type of compressor generally used is a rotary pump (of the Roots Blower type.) Oil being soluble in ethyl chloride cannot be used for lubrication, so pure glycerin is employed; this separates out by gravity without difficulty. The only serious difficulty in designing the plant is to make certain of avoiding leaks on the low pressure side; all air leaking in accumulates in the condenser and has to be purged from time to time. To avoid air leaks all valve spindles, compressor shafts, etc., have to be sealed with glycerin, so that any leakage is of glycerin not air.

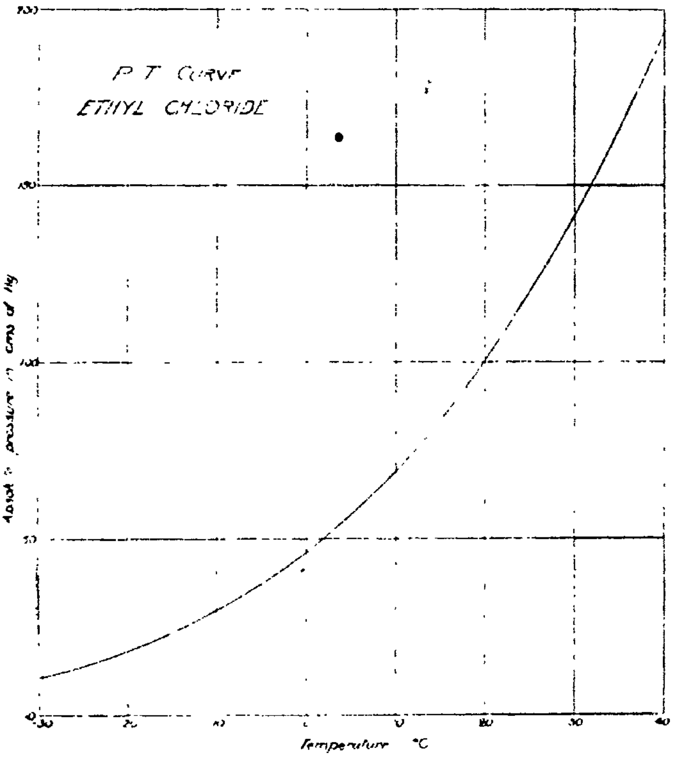

FIG. 1.

Owing to the low pressures the volume of the pump and the cross sections of the pipes are enormously larger than those in carbonic acid or ammonia plants. On the other hand the strength required is very little, which makes the machinery very safe.

Reciprocating pumps are not suitable for compressors because the piston rod, which is lubricated with glycerin, carries moisture into the pump every stroke. The writer has had great difficulties with his research plant from this cause.

The inflammability of ethyl chloride is its most serious drawback. To get over this various "non-flam ethyl chlorides" have been put on the market. These are mixtures of ethyl chloride with large proportions of methyl bromide. The mixture is not only non-inflammable, but may be used as a fire extinguisher. Its properties as a refrigerator are not very different from those of ethyl chloride, but as it is heavier than glycerin, special separators are necessary.

Impure ethyl chloride is supplied for refrigeration; it contains a small proportion of methyl chloride which may be slightly advantageous, as it raises the vapour pressure.

The writer is carrying out a complete investigation of the thermal properties of ethyl chloride for the Food Investigation Board (Department of Scientific and Industrial Research) and complete $\theta$-$\phi$ and I-$\phi$ charts will shortly be published.

## *DISCUSSION ON "LABORATORY METHODS OF LIQUEFACTION."*

**Professor C. F. Jenkin:** May I ask Dr. Crommelin the number of benches that can be accommodated with apparatus of this sort. I think it would be very interesting to know how many people can be doing work at these low temperatures at the Leyden Laboratory. Is it only possible for one or say twenty?

**Dr. Crommelin:** It is very hard to say a definite number, but it would be ten or twelve research students, or something like that. It depends entirely upon the kind of investigation.

**Dr. M. W. Travers:** Like many others I have been profoundly interested in Professor Crommelin's account of the work of the Leyden Laboratory, which I had the honour of visiting twenty years ago in company with Sir William Ramsay. In those days we were interested in low temperature research, but I am afraid if I showed on the screen pictures of our plant they would raise a smile. Our interest in liquid air and liquid hydrogen was the outcome of investigations connected with the rare gases of the atmosphere. We began our work without a liquefying plant, obtaining liquid air through the kind offices of Dr. Hampson and Mr. K. S. Murray, of what is now the British Oxygen Company, who was then commencing experiments, the development from which he has told us about this evening. Small quantities of liquid air, brought to our laboratory at seven o'clock in the evening, were our only supplies for the first nine months that we were engaged on this work. Early in the year 1899, Mr. Rose Innes presented the laboratory with a Hampson liquid air machine, and Dr. Ludwig Mond provided the funds for the purchase of a compressor, making it possible for us to carry out our work under reasonable conditions.

Later in this investigation it became clear that it would only be possible to obtain pure neon by separating it from argon and helium by means of liquid hydrogen. The problem of liquefying hydrogen without spending much more than £50 on the work fell to my lot. The liquefier was constructed from stock sizes of brass tube, punched blanks, etc., with only a single casting. The hydrogen was made in a beer barrel. An exhaust pump which formed part of the plant was a blowing pump, made by one of the students in his own workshop, with the valves reversed, and it was driven by a gas engine of a primitive type, borrowed from the engineering museum. However, the plant worked satisfactorily, and gave us sufficient liquid hydrogen for our purpose. Later, I reconstructed it, and carried out some researches at temperatures down to 14° K. That was in 1903, and since then my work has lain in other directions.

I want to ask one question, which arises out of Professor Porter's remarks. I always found that I got the best results with my hydrogen liquefier when the pressure at the top of the first cooling coil was about 120 atmospheres, or less. The pressure at the jet must have been lower. This was the pressure which was generally maintained at the gauge while the liquefaction of the hydrogen was actually proceeding. I may add that, on one occasion, when giving a demonstration of the liquefaction of hydrogen in Berlin, the gas was obtained from cylinders, and was successfully liquefied at a much lower gauge pressure. We tried working at higher pressures, but I never remember seeing the pressure indicated by the gauge standing at over 120 atmospheres while the liquid was running into the receiver. I should like to ask Professor Crommelin if he has observed an upper limit of pressure above which the cooling on expansion appears to diminish? I believe that he told us that the helium plant was run at a low pressure.

**Dr. Crommelin:** 25 to 30 atmospheres with the helium plant and 150 to 160 with the hydrogen plant.

**Dr. Travers:** Do you find that at 180 atmospheres you get a better or a worse result?

**Dr. Crommelin:** There is not much difference, even at 220 atmospheres the producing capacity is about the same.

**Professor Porter:** I do not expect hydrogen to lower at all in temperature in throttle expansion at any temperature if the pressure is higher than 240 atmospheres.

**Dr. Travers:** My next point is of practical importance. I was, at the beginning, very much afraid that the condensation of even small quantities of air would lead to blocking of the pipes and stoppage of the apparatus. Though my hydrogen undoubtedly contained traces of air, it gave me no trouble. On the other hand, when a block occurred, it was always traced to oil from the plant. Is that your experience, Professor Crommelin?

**Dr. Crommelin:** Blockings may occur on account of impurities in the gas or of oil vapour; we use oil separators, so that there is no trouble with the oil.

**Dr. Travers:** You take some precautions, however.

**Dr. Crommelin:** Yes, there are oil separators, but I am not quite aware of the details of their construction. There was in the beginning a good deal of trouble with the liquid hydrogen apparatus. If you worked the plant for half an hour it was all right. If you worked for a longer time then you had trouble. At the Reichsanstalt they had trouble when working for long periods, and they had to put in a heating spiral, so as to be able to heat the apparatus up, clear it, and then cool down again.

**Dr. Travers:** Professor Crommelin speaks of 13 litres of liquid hydrogen an hour. We never obtained more than ½ a litre, which was, in those days, a very large quantity.

**Dr. J. A. Harker:** I would like to say one or two words to endorse your expression of thanks to Dr. Crommelin for coming here this afternoon and giving us these very interesting papers. I was able, some ten years ago, to visit Leyden and see some of the things which he has described to us. I remember that on that occasion Professor Onnes and Dr. Crommelin were both present and I had the extreme pleasure of their own exposition of some of the things they were doing. One thing I remember—and it remained with me—which Dr. Crommelin has perhaps not sufficiently emphasised to-day, was the marvellous dependence of the epoch-making work that has been done at Leyden on extremely delicate and difficult apparatus-building, and more particularly on apparatus made of glass. One of the things that impressed me most at that time was something which Dr. Crommelin referred to this afternoon as a more or less ordinary matter—the use of vacuum vessels of extremely complicated construction, without which many of the results they have obtained could never have been reached. When at Leyden I was shown a piece of the helium plant, which was a vacuum vessel about as thick as one's little finger, bent round at a right angle. This was not a single vacuum vessel but it enclosed another concentric with it, the tubes of both being of egg-shell thickness. Anyone reasonably skilled can make a vacuum vessel of sorts, but it is quite another matter to make one vacuum vessel inside another

**Professor A. W. Porter:** There is only one point with which I want to deal, and that is in connection with the measurement of the extremely low temperatures to which we have been introduced to-night.

Professor Onnes has attempted to obtain the value of these extremely low temperatures (below 1 K) by plotting a curve of the reciprocals of the reduced temperatures against the logarithms of the reduced vapour pressures as far as the directly determinable values go and then extrapolating by means of a linear law.

I wish to suggest that it may be possible to obtain a truer extrapolation by means of one of the various theoretical curves which are adopted for representing vapour pressures. Approximately, for many substances at any rate, we can write,

$$\pi = a\gamma e^{-\frac{b}{\gamma}},$$

where $\pi$ and $\gamma$ are reduced pressure and temperature respectively; or since $\pi = 1$ when $\gamma = 1$, $\log_{10}\pi = \log_{10}\gamma - \frac{b'}{\gamma} + b'$.

On a curve with the same co-ordinates as Kamerlingh Onnes uses the slope will be,

$$-\frac{d\log\pi}{d\left(\frac{1}{\gamma}\right)} = b + \gamma;$$

hence it is greatest at the origin and diminishes as $\frac{1}{\gamma}$ increases—ultimately, but gradually, becoming straight.

I have determined the constant $b'$ in such an equation taking as fixed point the experimental point for $\frac{1}{\gamma} = 3$, so as to be well within the experimental region. The value of $b'$ is 8·46 and the curve is shown in the figure by a continuous line; Kamerlingh Onnes' curve is shown dotted. From the curve I have read off the temperatures corresponding to various pressures and tabulate them below along with values I am K. Onnes curve for comparison.

These remarks are only intended to indicate that it would be worth while specially to study the general form of the vapour pressure curve in the non-extrapolated region and to employ the information so gained to extend our knowledge of temperature values.

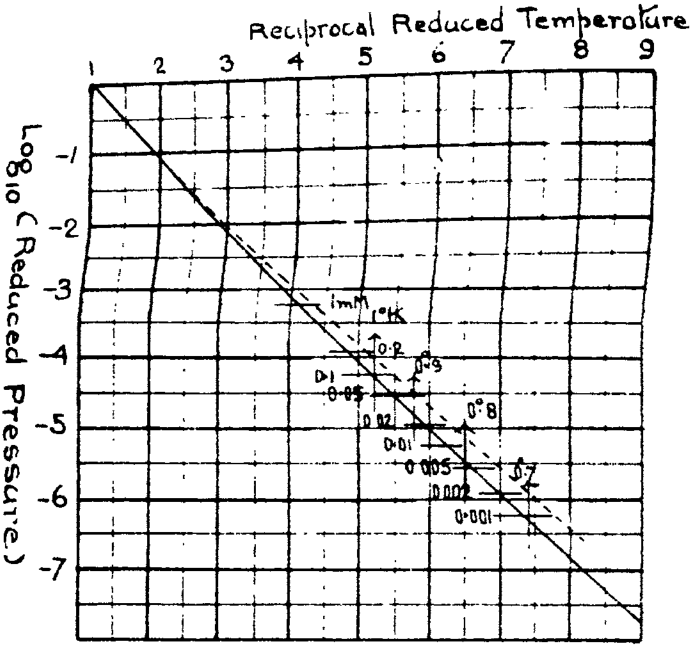

Fig. 1.

| Pressure mm. Mercury. | Temperature from K. Onnes. | Temperature from Porter. |
|---|---|---|
| 0·1 | 1 K | 1 K |
| ·05 | 0·89 | 0·94 |
| ·02 | ·82 | ·87 |
| ·01 | ·79 | ·825 |
| ·005 | ·74 | ·785 |
| ·002 | ·70 | ·74 |
| ·001 | ·65 | ·71 |

**Professor Kamerlingh Onnes** (*reply communicated. December 16th, 1922*): I quite agree with Professor Porter that it is of importance to study experimentally the vapour pressure curve in the non-extrapolated region to get better information on the temperature values in the lower one. There is a new investigation of this difficult subject in hand and

I trust we shall succeed in extending it to lower temperatures and in obtaining more accurate data than are available at present.

The present data seemed compatible with a curve that for lower reduced temperatures becomes finally rectilinear, in analogy with the cases given in Fig. 9, § 14. When this was the case, then by drawing the tangent to the experimental curve the values of temperature obtained would at least not be too low.

By extrapolation according to a theoretical formula of the form of that given by Professor Porter lower temperatures, and not as Professor Porter finds higher temperatures, were found. Professor Verschaffelt who calculated the formula which was used in this extrapolation had emphasised the theoretical meaning of

$$\log_{10} \pi = A + C \log_{10} \gamma - \frac{B}{\gamma}$$

by introducing into it for A the reduced chemical constant for helium, 0·59, and for C the theoretical value for monatomic gases, 2·5, and then fitting B to the observations. Assuming $\log_{10} \pi = -2·18$ for $\gamma = \frac{1}{3}$, according to the plotting, one finds $B = 0·53$; so we should have, below $\gamma = \frac{1}{3}$,

$$\log_{10} \pi = 0·59 + 2·5 \log_{10} \gamma - \frac{0·53}{\gamma}.$$

The temperatures read from the curve represented by this formula, *viz.*:

| | |
|---|---|
| 0·1 | 0·94 |
| ·05 | ·87 |
| ·02 | ·80 |
| ·01 | ·75 |
| ·005 | ·70 |
| ·002 | ·65 |
| ·001 | ·62 |

are even lower than those found by rectilinear extrapolation. So the results, as I said, indicate that with the linear extrapolation we were on the safe side.

Differences of some hundredths of a degree such as occur between the results of Professor Porter and of myself are after all to be considered as within the limit of uncertainty of the experimental data from which we have to start.

# PART II. — INDUSTRIAL METHODS OF LIQUEFACTION AND PRACTICAL APPLICATIONS OF LOW TEMPERATURES.

**Mr. George Goodsir, President** of the British Cold Storage and Ice Association, opened this section of the proceedings with the following remarks :-

Before calling on the authors who are going to give us their papers, I want to say a word or two on behalf of the Society which I represent. First, I would like to express their best thanks to the Faraday Society for the honour they have done us in inviting us to meet with you and confer upon the subject of low temperatures. The Society which I represent is, in name, quite new, because this is practically the first official gathering under the name of the British Cold Storage and Ice Association. It is an amalgamation of two Societies which have been in existence, the one since 1910, and the other since ten years later. Their members are largely engaged in practical engineering, ship-owning and general refrigerating business and store keeping of various kinds, and its interests do not, therefore, compete in any way with the Faraday Society which is interested in the scientific side of refrigeration. I am afraid that when the discussion comes to deal with liquid air and such matters, we may find ourselves a little out of our depth. The temperatures which you handle quite unconcernedly are far beyond our wildest imaginations in the nature of cold, and our lowest temperatures are mere summer coolness beside what you are accustomed to speak about. Some day, perhaps, liquid air and other recent products of science may be made available for the ordinary work of the preservation of perishable food, but I do not think that is just yet. Meantime, this discussion which is to take place to-day may, perhaps, open our eyes to the possibilities in that direction, and although our members may not, many of them, be able to assist you very practically in the discussion, we will listen and learn, I am sure, and we will do what we can to add to the knowledge on the subject which may spring from our practical experience. With these few preliminary remarks I have pleasure in calling upon Mr. K. S. Murray, a gentleman well acquainted with the practical liquefaction of air for many years past, to open this section of the proceedings.

# INDUSTRIAL METHODS OF LIQUEFACTION AND PRACTICAL APPLICATIONS OF LOW TEMPERATURES.

By K. S. Murray, M.I.Mech.E.

The title of this paper was not selected by myself. Were I to deal with every subject which might legitimately be collected under such a comprehensive umbrella, I should require far more time than has been allotted to me. I have therefore decided to deal only with the subject of the separation of the constituents of air, with special reference to low temperature liquefaction.

When people talk of separating the constituents of the air, nine out of every ten have in view only the extraction of oxygen from the atmosphere, and, as I have been engaged in extracting vastly more than my fair share for the last thirty-five years, the subject is one on which I should be able to speak with some degree of authority. In fact, the history of the British Oxygen Company, with which I have been associated for the whole of that period, is so intimately bound up with the industrial development of oxygen that it is impossible, at any rate for me, to consider these subjects apart.

Therefore, for historical accuracy, before dealing with low temperature extraction of oxygen from the atmosphere, I propose to refer very briefly to the barium oxide process for effecting the same purpose, as it was undoubtedly by that process, in the hands of the British Oxygen Company, that the oxygen industry was founded.

The British Oxygen Company was established in 1886 as the Brins Oxygen Company, to take over an alleged process for the production of oxygen, patented by two French brothers whose name was adopted as the title of the Company. The Brin process was based on Boussingault's discovery in 1851, that at a temperature of about 540° C. the monoxide of the metal barium would absorb oxygen readily from the atmosphere with the resulting formation of dioxide, and that at a higher temperature of about 870° C. the oxygen thus absorbed would be given off again and the barium restored to the monoxide condition ready for the cycle to be repeated.

As a natural consequence of Boussingault's discovery many efforts had been made to establish a commercial process for the production of oxygen based on this apparently unalterable property of barium oxide. In spite, however, of its chemical simplicity, many practical difficulties arose which remained unsurmounted until the advent of the Brins Oxygen Company. Even then it was only after prolonged and costly experimental work which resulted in the Brin process being practically thrown overboard, that the barium method of abstracting oxygen from the atmosphere became an established success. I described the process fully in a paper I read before the Institution of Mechanical Engineers on January 31st, 1890, and I cannot do better than refer to that paper anyone who may be still interested in the process.

Here it is sufficient to say that the fundamental changes which we effected were: (1) working at a constant furnace temperature of about 650° C., change of pressure being relied upon for determining the respective

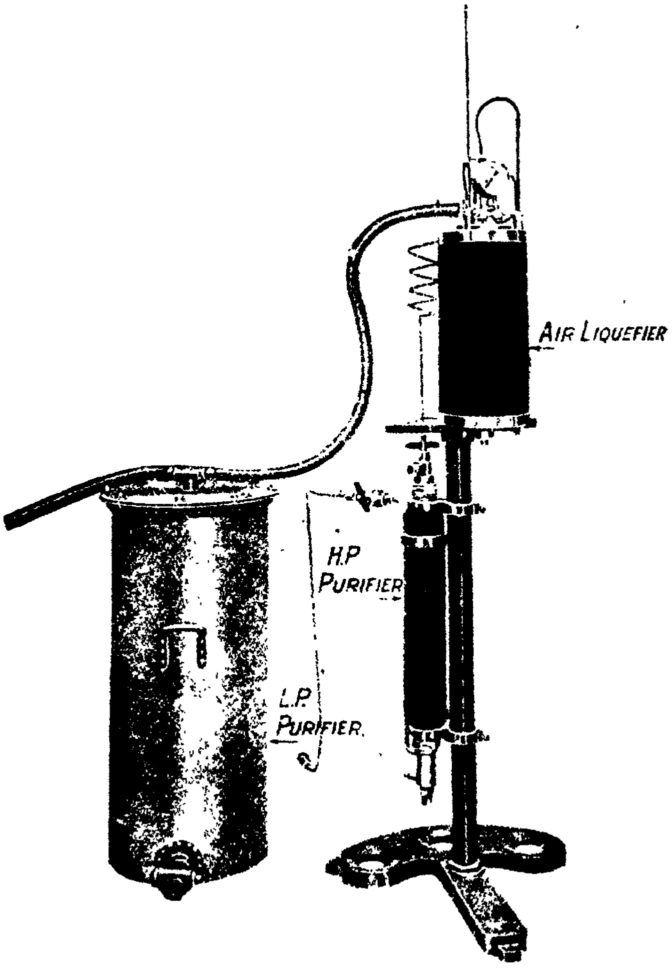

FIG. [illegible] Hampson's Air Liquefier.

phases of oxidation and reduction; (2) short operations lasting only a few minutes each; (3) the automatic reversal of the various valve gears necessary in operating the process.

The process was exclusively employed by the British Oxygen Company for nearly twenty years in their London, Birmingham, Manchester, and Glasgow factories, and a considerable number of plants, varying in capacity

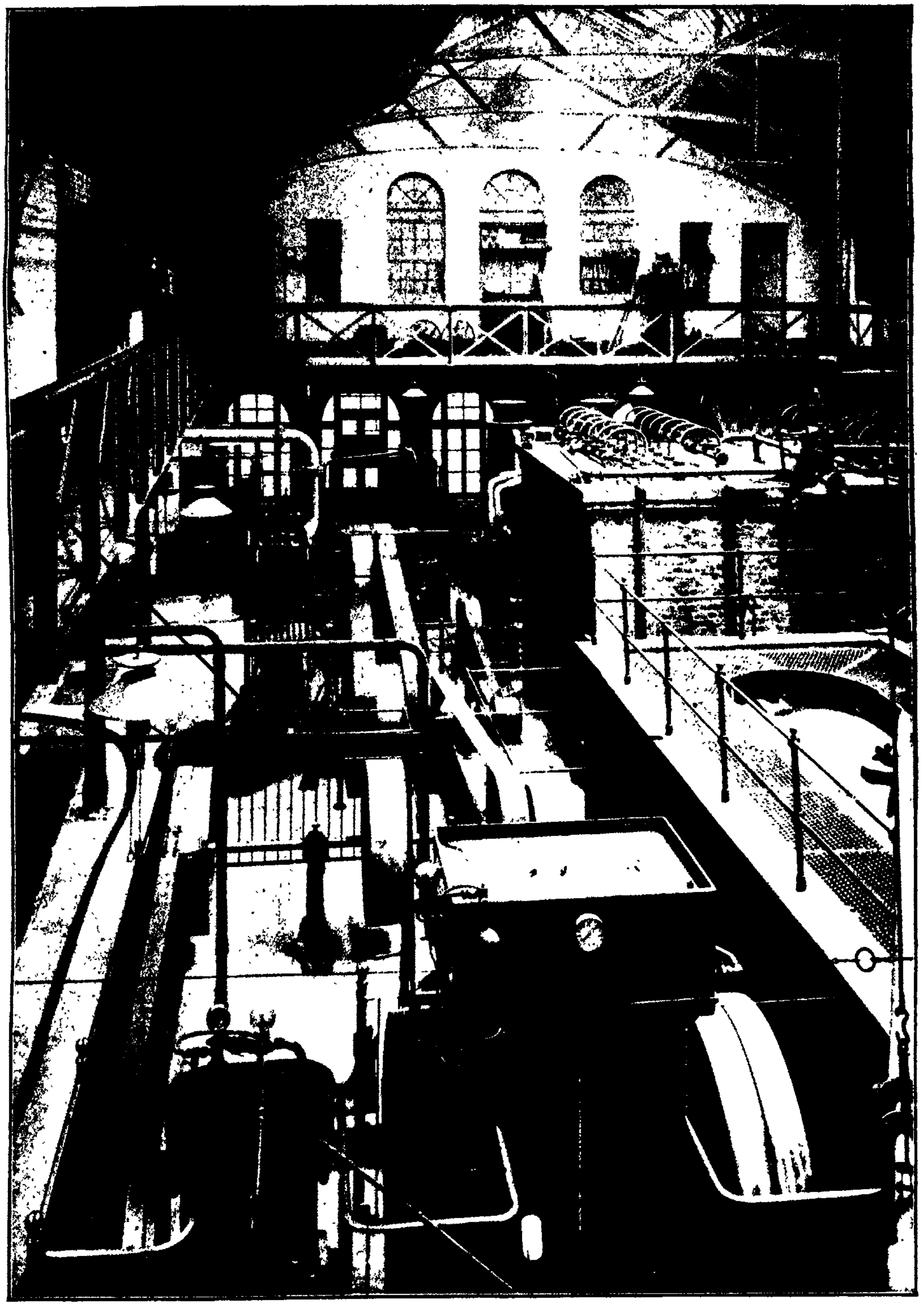

FIG. 2.—Westminster Works, B.O. Co., 1906.

[*To face page* 207.

from 5000 to 30,000 cubic feet of oxygen per day, were also erected by them to provide oxygen for industrial applications. A fact which is especially worthy of mention is that the first plants for the commercial production of oxygen in Paris, Berlin, and New York, were of the barium oxide type and were erected by the British Oxygen Company.

I am afraid not a single barium plant remains in existence to-day although in point of economy the process does not compare unfavourably with liquid oxygen plants of the smaller type, and it was abandoned mainly because it was incapable of producing oxygen of equal purity.

As early as 1896 the British Oxygen Company, as the makers of Hampson's apparatus for the liquefaction of air, became connected with low temperature research. The Hampson apparatus (Fig. 1), which is based on a nozzle, or free internal, expansion, is so efficient in its temperature interchange, that when expanding about 700 cubic feet of air from a pressure of 150 atmospheres to atmospheric pressure, it begins to produce liquid in about 6 minutes with a yield of about 1 litre of liquid per hour.

For the production of liquid air on a commercial scale, this apparatus is too small to be of any value. On the other hand it is specially designed for the quick production of liquid for research purposes and it has been adopted for that purpose in many educational establishments and research laboratories throughout the world.

The success which attended the introduction of this apparatus, coupled with the still more important work of Professor Carl von Linde in the liquefaction of air, pointed to a method for the separation of its constituents which might develop into a rival to the barium process; consequently, the British Oxygen Company, like other concerns equipped with facilities for the production of liquid air, were quietly experimenting between 1896 and 1903 with various methods for separating the constituents of liquid air by partial evaporation.

It must, however, be admitted that the problem remained entirely unsolved until the process of rectification was disclosed by Professor Linde in the latter year. From that date onwards rectification has been the fundamental principle underlying every patented method for separating the constituents of liquid air.

The British Oxygen Company were not long thereafter in realising that their barium process for producing oxygen was at length seriously threatened by the introduction of rectification for separating the constituents of liquid air. We therefore concluded an arrangement with Professor Linde under which we acquired his British and British Colonial rights in rectification.

In 1906 we erected in our Westminister Works a Linde plant capable of producing about 500 cubic feet of oxygen per hour. It is illustrated in the photograph, Fig. 2.

This photograph is of some general interest, because it shows on the left-hand side the first liquid air plant erected for the production of oxygen in this country, and on the right-hand side a portion of the last, and best, of many barium oxide plants erected by the Company. Professor Linde himself was so struck with the efficiency and mechanical simplicity of this latter plant that, largely on his recommendation, the two plants were worked side by side for many months before it was finally decided to substitute liquid air for barium oxide plants in the production of oxygen throughout the Company's factories.

In 1908, as the outcome of prolonged litigation, which established Linde's claim to the rectification of liquid air, the Company entered into an agreement with the Société l'Air Liquide of France under which we acquired the Claude British and British Colonial patents (with the exception of Canada), for the separation of oxygen and nitrogen from liquid air. In many of our factories we have to-day Linde and Claude plants working side by side. We therefore claim to have had exceptional facilities for comparing the two systems on which the important oxygen industry of to-day has been developed in all parts of the world.

I now propose to describe and illustrate diagrammatically the essential features of the Linde and Claude systems, and as I am dealing with the subject from the industrial rather than the scientific point of view, I shall confine myself mainly to facts and figures which are based on practical experience. I must therefore assume the production of liquid air to have reached the stage where Linde's adaptation of the Joule-Thomson effect and Claude's expansion engine enabled that liquid to be produced in commercial quantities. I must also assume the physical laws involved in its production to be generally understood.

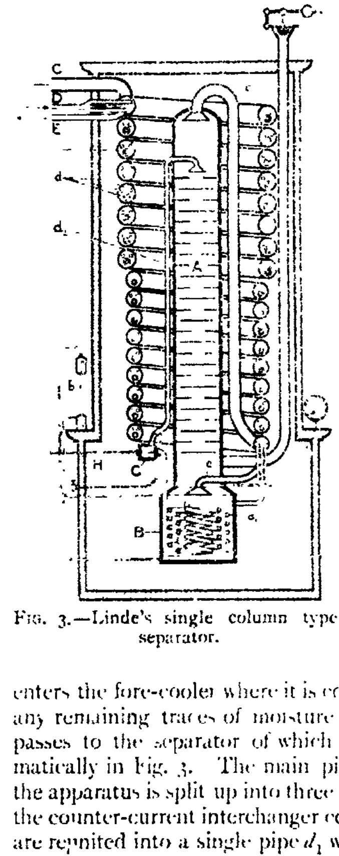

Fig. 3.—Linde's single column type separator.

The Linde plant shown on the left of Fig. 2 represents the earliest type employed for the separation of oxygen from liquid air. Such plants consist essentially of an air compressor; a suitable purifier for eliminating carbon dioxide; a drier for removing moisture from the air; a fore-cooler, which is kept cold by means of an ammonia or a carbon dioxide machine; and finally, the separator containing the counter-current heat interchanger and the rectification column.

The working of such a plant is as follows: Air is drawn by the compressor through a lime or caustic soda purifier in order to remove carbonic acid. It is then compressed, under conditions as nearly isothermal as possible, to a pressure of about 135 atmospheres and passed through a drier containing calcium chloride in order to remove moisture. It then enters the fore-cooler where it is cooled to a temperature of about −30 C., any remaining traces of moisture being deposited there as ice, and finally passes to the separator of which a sectional elevation is shown diagrammatically in Fig. 3. The main pipe D conveying this compressed air to the apparatus is split up into three small pipes *d* at the point where it enters the counter-current interchanger coil C. It passes down these pipes, which are reunited into a single pipe $d_1$ when they leave the interchanger and this pipe $d_1$ which is coiled in the vaporiser B as shown, is attached to the inlet of the valve G. At this point, by the adjustment of the regulating valve spindle H, the air is caused to expand from a high to a low pressure and is discharged at this low pressure through the rose-ended pipe $d_2$ into the top of the rectification column A. The expanded air fills the column and then flows through the only two possible outlet pipes *c* and *e* which surround the small pipes *d* thus forming a counter-current interchange of heat, as the outgoing expanded air ascends the interchanger coil through which the high pressure air is descending in the small pipes *d*. The expanded cold gases, having thus abstracted heat from the incoming compressed air, leave the separator at C and E as indicated in the diagram, nearly at atmospheric temperature.

It is at the valve G that Linde obtains the Joule-Thomson cooling effect and this is made cumulative by means of the counter-current heat interchanger. The apparatus is completely enclosed in a wooden casing and all spaces are packed with suitable insulating material, consequently, after starting the plant with everything at atmospheric temperature, the separator gradually cools down until some of the expanded air begins to liquefy and collect round the coils in the vaporiser B. The quantity of liquid thus collected is registered outside the apparatus by means of an ordinary coloured liquid which is contained in a glass tube *b* enclosed in a pressure equalising circuit as indicated. Once this stage is reached liquid begins to accumulate rapidly in the vaporiser B, and the initial pressure of the compressed air may be gradually reduced by increasing the opening of the valve G.

As the liquid begins to accumulate round the coils in the vaporiser B, the compressed air transmits some of its latent heat to the liquid. The latter is thereby evaporated whilst the compressed air is itself liquefied in proportion to the amount of heat thus extracted. The vapours thus produced flow upwards through the rectification column A whilst the liquid formed in the compressed air pipe coil $d_1$ ascends through the pipe $d_2$ and is discharged through the rose-end at the top of the rectification column. The temperature gradient necessary for efficient rectification then rapidly becomes established in the column, and the final stage is reached under which the separation of oxygen is effected. The pipes C and E of the counter-current interchanger then begin to fulfil their proper functions, the nitrogen vapours being delivered through the former from the top of the column and the oxygen vapours through the latter from the top of the vaporiser. The separated gases leave the apparatus at C and E respectively at or near atmospheric temperature, having abstracted heat from the incoming compressed air whilst passing up the counter-current interchanger.

The action which takes place in this, the simplest type of rectification column, must now be briefly explained as exactly the same principle is involved in all others.

Linde relies for his temperature gradient on the difference between the boiling point of nitrogen and oxygen. The former is − 196° C., and the latter − 183° C. Liquid air is discharged into the top of the column at an intermediate temperature of about − 194° C. As it passes down nitrogen, being the more volatile component, immediately begins to evaporate off and the liquid gradually becomes richer in oxygen, with a somewhat higher temperature. As this rich oxygen liquid accumulates in the vaporiser it is evaporated by the compressed air passing through the coil until it is practically pure oxygen with a temperature very nearly − 183° C. There is thus a temperature gradient of about 11° C. established between the top and the bottom of the column. Liquid air passing down the column is brought into intimate contact with the rising vapours of oxygen and an exchange of material takes place. At each stage some of the rising oxygen is condensed and some of the nitrogen in the descending liquid is evaporated, whilst the liquid gradually gains in temperature until by the time it reaches the vaporiser its composition is that of practically pure oxygen. The gas on the other hand which passes off from the top of the column through pipe C is mainly nitrogen at a temperature about $11^{\circ}$ C. lower than that of the oxygen at the bottom of the column. The oxygen which rises in the column to effect the material exchange with the nitrogen of the descending liquid, is carried back to the vaporiser together with most of the oxygen contained in the original liquid; thus there is a constant accumulation of oxygen which passes off as vapour through the pipe E. The gases taken separately from the top and bottom of the apparatus through the counter-current interchanger, are made to abstract heat from the incoming compressed air on its way to be liquefied.

When normal oxygen-producing conditions are established, the air supply from the compressor becomes reduced from 135 atmospheres to about 55 atmospheres, the latter pressure being found sufficient to make good all thermal losses due to friction, leakage of heat from outside, and imperfect interchange in the counter-current system.

This type of separator is easy to operate and from an economical point of view has been found satisfactory hitherto for use in relatively small oxygen producing plants. A defect, however, of rectification in this form is that although oxygen of high purity can be produced, at least 7 per cent of oxygen is contained in the waste nitrogen. Baly's well-known experiments in 1900 demonstrated that the vapour in equilibrium with any liquid mixture of oxygen and nitrogen always contained more nitrogen than the liquid and that when the evaporating liquid is air, the proportion of oxygen present in the vapour is 7 per cent. Therefore, in a rectification column, such as this early Linde type, where liquid air enters at the top a loss, amounting to about one-third of the oxygen in the air, is inevitable.

With large plants this becomes a serious matter, and I believe I am correct in stating that Claude was the first person to design a separator which obviates this loss. I will, therefore, now, in order to maintain chronological accuracy, briefly describe a type of Claude plant capable of producing 4,000 cubic feet of oxygen per hour, which is largely employed by the British Oxygen Company at the present time in nearly all of their factories in this country.

The outstanding features of Claude's plants are: (1) Cooling by means of an expansion engine. (2) A selective system of rectification rendered possible by a preliminary partial separation of oxygen and nitrogen. (3) A combined system of heat interchange and drying which renders chemical abstraction of moisture from the air unnecessary.

The working of the plant is as follows: Air is drawn by a compressor through purifiers to remove carbon dioxide as in the Linde plant. It is then compressed to a maximum pressure of about 33 atmospheres and passed through two vertical tubular heat interchangers in series. In passing through the second of these it meets in counter-current the cold separated oxygen and nitrogen passing outwards from the separator and a very complete interchange of heat takes place. Here also most of the moisture is thrown down as water and drawn off at intervals, the remainder being arrested in the form of ice round the tubes at the top of the interchanger. Meanwhile the first interchanger which had previously performed the same function, is being thawed out by the air passing through it, in order to be ready for subsequent use. Thus these interchangers are operated as such alternately, being changed over at intervals of 8 hours. The compressed air leaves the second interchanger at a temperature of about − 100° C. 60 to 70 per cent. of the cooled air goes direct to the expansion engine where, in expanding to about 4 atmospheres, it performs external work against a dynamo brake and issues from the engine at a temperature not far removed from its point of liquefaction. The remainder of the air passes under full pressure into an interchanger, termed the liquefier, where it is liquefied by meeting in counter-current all the cold oxygen and nitrogen passing from the separator to the second, or operating, interchanger previously described. The cold vapour from the expansion engine and the liquid from the liquefier both enter the outer compartment A of the liquid collecting vessel shown in the diagram (Fig. 4) at the bottom of the vaporiser, the liquid supply being controlled by the valve shown, which performs the same function as the valve G in the Linde apparatus already described.

By this skilful combination of internal and external expansion, Claude is able to obtain a high efficiency from his expansion engine. For this latter purpose it is obviously desirable to keep the compressed air as warm as possible. By passing the cold gases through a liquefier a twofold purpose is served. First, a moderate supply of liquid air for making good cold losses is assured by very effective heat interchange, coupled with the Linde method of internal expansion. Second, the heat usefully abstracted by the cold gases from the compressed air passing in counter-current through the liquefier, raises their temperature to a point which prevents them abstracting, at a later stage, too much heat from the compressed air passing through the main interchanger to feed the expansion engine.

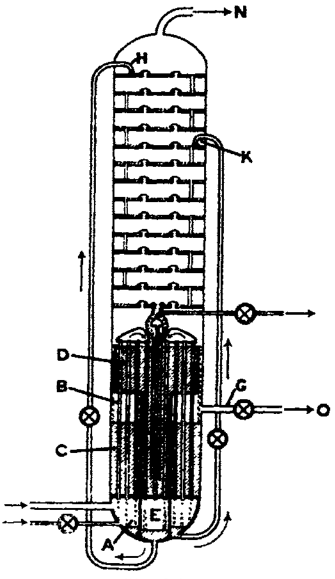

FIG. 4.—Claude's separator.

Reverting to the diagram, it will I hope now be obvious that a regular and adjustable supply of liquid air and intensely cold vapour is fed to the outer compartment A below the vaporiser. The vapour thus ascends the vertical nest of tubes B (leading from the top of this compartment), which are immersed in baths of liquid oxygen C and D. In these tubes the vapour undergoes progressive liquefaction and oxygen being the less volatile constituent, it is the more readily condensed and flows back as liquid into the compartment. A partial scrubbing effect, or rectification, also takes place, consequently the vapour passing out at the top of the tubes is very rich in nitrogen. This rich nitrogen vapour travels down a similar nest of tubes leading to the inner compartment E of the bottom vessel which it reaches partly in the liquid condition. Thus in practice liquid containing about 40 per cent. oxygen is obtained in the outer compartment and liquid containing about 4 per cent. oxygen is obtained in the inner one. A pressure of 4 atmospheres is necessary in these compartments, and the tubes communicating with them, in order to raise the liquefying point of the oxygen-nitrogen mixtures above − 183° C., the temperature of the liquid oxygen bath, so that liquefaction may take place and that latent heat may pass to the liquid oxygen and evaporate it to a corresponding extent. Above the vaporiser, as in the Linde apparatus, is the rectification column. The liquid, rich in nitrogen, is conveyed from the inner compartment E to the top of the column at H. The liquid containing about 40 per cent. oxygen is conveyed from the outer compartment A to the column at the point K where the composition of the ascending gases should correspond to that of a gas mixture in equilibrium with a 40 per cent. oxygen liquid. Rectification with the correct temperature gradient then proceeds as already described in connection with the Linde separator (Fig. 3) with however the important difference that, as rich liquid nitrogen replaces liquid air at the top of the column, a correspondingly lower temperature is maintained there, thus extending rectification, with the result that nearly all the oxygen is abstracted from the air. The waste nitrogen is taken away to the liquefier interchanger from the top of the column and oxygen through the pipe G above the lower of the two communicating oxygen baths, which latter are so arranged that a uniform supply of good quality is assured.

An interesting addition to the separator is a small nest of tubes in the centre of the vaporiser through which a quantity of rich nitrogen from the inner compartment E can be withdrawn as indicated. After this additional scrubbing a relatively small, but useful, quantity of gaseous nitrogen of 99·5 to 100 per cent. purity, can be obtained as a by-product.

All parts of the apparatus subject to temperatures below that of the atmosphere, are efficiently insulated and when working conditions are established, air is delivered by the compressor at a pressure of 26 atmospheres. 33 atmospheres, already mentioned as the maximum pressure, is the initial pressure employed to hasten cooling down. This is less than a quarter of the initial pressure required by Linde and other plants, which is not only a fine tribute to the efficiency of Claude's expansion engine, but this relatively low maximum pressure enables lighter material and more efficient design to be employed in the interchangers and elsewhere.

A striking feature of the expansion engine is that it works without any cylinder lubrication. Specially treated leather, from which water and fatty matter have been removed, is employed as piston packing and it is found that, at the low temperatures involved, leather in this condition remains pliable and the engine gives no more trouble than an oil lubricated machine.

We find that these plants under daily working conditions produce oxygen of 98·5 per cent. purity for an expenditure of about 185 B.H.P. per hour or 46 B.H.P. per 1000 cubic feet of oxygen. The labour required for working the plant is no more than is required for a plant one-tenth the size. We do not employ larger plants than these as we find them to be a unit of convenient size for our oxygen factories.

We do not employ Linde plants of larger capacity than 2000 cubic feet of oxygen per hour, but so far as the separator is concerned, these and all larger Linde plants are now similar in most respects to the Claude design.

In producing cold with these larger plants, Linde does not employ an expansion engine doing external work but still relies on the Joule-Thomson effect produced by internal expansion of the air. On the other hand he economises power by compressing only one-third of the air used to a constant pressure of about 135 atmospheres and the remaining two-thirds to 4 atmospheres. Thus like Claude he admits liquid and gaseous air to his separator and appears to obtain similar results with very little more expenditure of power. Fig. 5 is a diagrammatic illustration of Linde's separator.

This consists of two rectification columns, one above the other. The lower, like the condenser tubes in Claude's apparatus, works under a pressure of 4 atmospheres and the upper under atmospheric pressure. The high pressure air at 135 atmospheres enters the bottom vaporiser at C and is liquefied in exactly the same manner as in the single apparatus illustrated in Fig. 3, entering the lower column, after expansion, through the rose-end shown. This supply of liquid air, like that of the Claude liquefier, makes good all cold losses. The low pressure gaseous air enters the bottom vaporiser at B and passing through a separate coil is discharged into the lower column about the centre, as shown, from which point it rises to a nest of tubes D surrounded by a bath of liquid oxygen, as in the Claude apparatus. Here partial liquefaction takes place, and the liquid falls back over the plates with a scrubbing effect on the rising vapours. Most of the oxygen is thus removed and accumulates as liquid in the lower vaporiser. The remaining gas, practically pure nitrogen, passes over to be condensed in the external tubes as indicated. Thus liquids, rich in nitrogen and oxygen respectively, are supplied as in the Claude apparatus to the upper column, in the positions shown, for final rectification. Both nitrogen and oxygen are drawn off as indicated through a counter-current coil interchanger similar in construction to that shown in Fig. 3, in order to abstract heat from the incoming high and low pressure supplies of air, the whole being similarly insulated. In these plants, as in the smaller, Linde employs an auxiliary fore-cooler which is kept cold by an ammonia or carbon dioxide machine, but he also employs the fore-cooler for separating out moisture from the air.

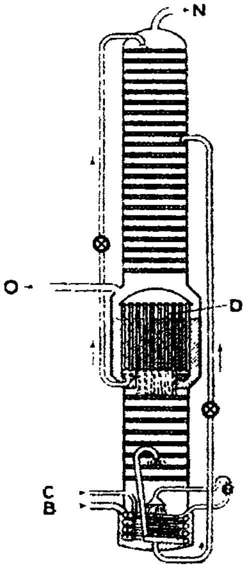

Fig. 5.—Linde's double column type separator.

I am not able to speak from personal experience of a Linde plant of greater capacity than 2000 cubic feet of oxygen per hour. This latter plant, however, absorbs about 106 B.H.P. per hour, or 53 B.H.P. per 1000 cubic feet of oxygen produced. Both Linde and Claude oxygen separators have been manufactured up to a capacity of about 9000 cubic feet of oxygen per hour. With such plants the power consumed per 1000 cubic feet of oxygen produced, is about 33 B.H.P. I believe the Linde Company have also manufactured larger units, for which they claim still lower consumption of power, but the design and construction of efficient heat interchangers for large oxygen plants is likely to put a limit to their size and I venture to doubt whether a plant with much lower consumption of power than 30 B.H.P. per 1000 cubic feet of oxygen is possible with due regard to economy in other directions.

Whilst on the subject of large plant units, reference may appropriately be made to the well-advertised Jeffries Norton process which we have repeatedly been assured would produce oxygen at 6d. or less per 1000 cubic feet.

The process appears to be based on the fact that heat interchange should take place between high pressure gases, in order to recover power by expansion more effectively than is the case in existing systems, where heat is transmitted from a high to a low pressure gas.

In Fig. 6 I give a very free diagrammatic illustration of the process as I understand it. Air at a pressure of say 20 atmospheres enters the system at A and on its way to the rectification column B (which is operated at only a slightly lower pressure) it is made to pass through two interchangers, as diagrammatically illustrated, in order to heat up outgoing nitrogen and oxygen. The former of these first passes through its interchanger under full pressure. It is then split up as shown, about 60 per cent. being heated by suitable external means at D to a temperature of about 550° C. This hot and fully compressed gas then passes to a motor E, which it drives, generating sufficient power, it is claimed, to work the whole system. The remaining 40 per cent. of nitrogen, in order to help in counteracting heat influx, is expanded in the engine C, the expanded gas on its way out of the system being again employed as shown to abstract heat from the incoming compressed air. The separated oxygen leaving the rectification column under pressure passes as shown, to the expansion engine P, and the expanded oxygen on its way out of the system, is employed to abstract heat as indicated from the incoming compressed air.

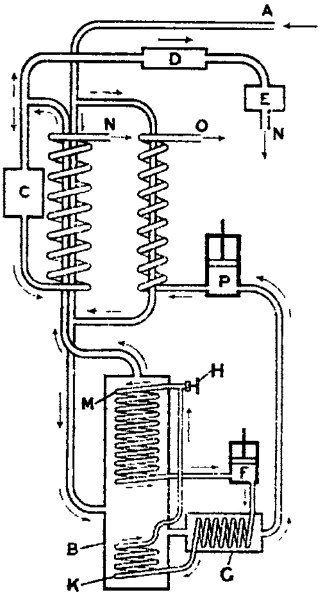

Fig. 6.—Diagram of the Jeffries Norton process.

I have already shown that in order to maintain the correct temperature gradient in rectification columns, it is necessary to have oxygen vapours at the bottom and nitrogen vapours at the top, but when the pressure in the column is nearly the same as that of the compressed air entering it, then the condensation of the latter in liquid oxygen cannot be effected and normal rectification cannot be set up. In order to get over this difficulty and transfer heat from the top to the bottom of his column, Norton places a coil K in the liquid oxygen bath at the bottom of the column through which an independent supply of oxygen, raised by the compressor F to a pressure above that prevailing in the column, is caused to flow after being first cooled by the outgoing oxygen vapour in G. The circulating oxygen is then condensed in the oxygen bath and afterwards expanded through the valve H to a temperature low enough to condense nitrogen. It is then drawn through the coil M to be recompressed by the compressor F in the enclosed circuit.

The Norton process has had the advantage of Government support in the U.S.A. where a large plant for the separation of helium from natural gases was erected in Petrolia, Texas. The plant was never successful and I understand it has now been abandoned, a plant erected by the Linde Air Products Company of the U.S.A. during the war at Fort Worth, Texas, being employed instead. I have not heard of any Norton plant being successfully operated for the production of oxygen and although the process has clever features and is refreshingly original, I am afraid most engineers who have had experience with very low temperatures, will regard it as somewhat impracticable.

There are many other makers of oxygen plants to-day, mostly of small size. Nearly all are based on the original Linde apparatus (Fig. 3) and I am not aware of any possessing novelty in design. Only one maker that I know of employs the Claude expansion engine. In that case, some of the air from the main compressor at a very high pressure and without previous cooling below atmospheric temperature, is sent through the expander and then through a heat interchanger to the centre of the column. This has certain advantages in the production of liquid air but I do not think it can be economically adapted to the production of oxygen. It is apparently claimed as an advantage of the system that ordinary oil can be used for lubricating the cylinder of the expansion engine. It is, however, a greater advantage of the Claude system that oil need not be used at all.

Cylinder lubricating oil is a source of trouble in liquid oxygen plants in two respects. (1) Traces are always liable to be carried forward and tend to foul up both interchanger pipes and the column, thus necessitating periodical and difficult cleaning. (2) The other, and more serious trouble, is in connection with the air compressor cylinders. The heat generated in each stage of compression, in spite of very efficient cooling, necessitates the use of special high flash point oils and precautions to ensure that the flash point temperature is not exceeded. It has been proved, however, that any lubricating oil heated in the presence of compressed air beyond its flash point, breaks down into simpler substances including free carbon and acetylene. These substances, particularly acetylene, are liable to be carried forward in the air and to accumulate as solid particles in liquid oxygen baths, thus producing conditions which have given rise to numerous explosions which have been almost invariably traced to the presence of acetylene. In our oxygen factories, until the cause became obvious, these incidents were amongst the most disquieting of our experience, but since we have got to the root of the trouble, we have greatly reduced the risk by introducing suitable safeguards on our air compressors. We have also taken precautions not to store carbide or use acetylene within 100 yards of our air intake. Thus we are forced to be very inhospitable in our own factories to a gas which has otherwise proved a valuable business ally.

Hitherto I have dealt only with plants producing a gaseous oxygen product. Liquid oxygen can always be drawn from such plants but they are not the most convenient construction for the purpose.

It is obvious that when some of the oxygen is drawn away in the liquid state its value in the interchangers for abstracting heat from the incoming air is lost. This has to be compensated for by increased pressure. Hitherto the demand for liquid oxygen has been practically restricted to rescue work and aircraft uses, but its employment for explosives, developed by the Germans during the war, is likely to extend and create a demand for plants primarily designed to produce liquid oxygen. The Société l'Air Liquide recently supplied a plant for this purpose to certain mines in Lorraine where German plants had hitherto been used. It works at a pressure of 60 atmospheres and produces 75 litres of liquid oxygen per hour for an expenditure of 140 B.H.P.; less than 2 B.H.P. per litre. We are also supplying to South Africa a much smaller plant working at a higher pressure which will produce liquid oxygen for an expenditure in power of 2·5 B.H.P. per litre and will alternatively produce gaseous oxygen. These results compare favourably with any others I have seen, but I am hopeful that we shall still further improve upon them in the near future.

The price of oxygen in the liquid state must always be more than in the gaseous owing to the greater expenditure of power involved in its production and losses due to evaporation in its use. We sell the liquid at infrequent intervals and small quantities, as drawn from the oxygen plants in our factories, at prices down to 1s. 4d. per lb. in Dewar vessels of small capacity, but to a regular and large consumer very much better terms could now be offered.

In Lorraine, where I have seen liquid oxygen extensively used in the iron mines for blasting purposes I was told that it cost 1 fr. 50 per litre, which, at the rate of exchange prevailing at that time, corresponded to about 7d. per litre in this country. Either of the liquid oxygen plants to which I have just referred would be easily capable of producing the liquid at this figure.

In recent years, thanks to improved methods of constructing metallic Dewar flasks, the transport of liquid oxygen has become much simplified. In flasks of 25 litres capacity and upwards the loss due to ordinary evaporation I am told should not exceed 5 per cent. in 24 hours, although in the mines a much larger percentage is of course lost by evaporation whilst the cartridges are being impregnated with the liquid immediately before they are used.

As regards the cost of gaseous oxygen, this varies with the size of plant employed to a larger extent than in the case of the liquid. As evidence of the extent to which this occurs it is only necessary to compare the cost of producing gaseous oxygen by means of present day liquid air plants of maximum and minimum sizes. For this purpose a plant producing 500 cubic feet of oxygen per hour may be taken as the smallest practicable unit, and for the other extreme I will take a Claude plant producing 9000 cubic feet of oxygen per hour, for that is the largest size of which I can speak with adequate personal knowledge.

Assuming power in each case to cost 1d. per B.H.P. (a somewhat high figure for the larger plant) then working continuously to their full capacity, with adequate power, labour, material and a fair proportion of all the usual standing charges, including interest on capital and depreciation, the cost of oxygen produced by the small plant would be 19s. and by the large one 4s. 6d. per 1000 cubic feet.

If these plants were worked intermittently so as to produce annually only half of their full output, the standing charges would tell greatly in favour of the large plant. I estimate that the cost of oxygen would then be with the small plant 27s. and with the large 6s. 3d. per 1000 cubic feet.

These costs are for gas into the gasholder. In the case of oxygen factories supplying the gas in cylinders it is obvious that with requisite supervision, heavier overhead charges, relatively small plants in operation and a fluctuating demand the cost of oxygen must always be very appreciably higher than in works where the gas can be used direct from the holder.

Throughout their factories in this country the British Oxygen Company have now plant capable of producing an aggregate of 2 million cubic feet of oxygen per day. Our present sales fluctuate between 4 and 5 million cubic feet per week, which is less than half the total capacity of our plants. Our present average price for oxygen in cylinders is about 38s. per 1000 cubic feet, although to many large consumers the price is substantially lower.

This price I believe compares favourably with that prevailing in other countries with the probable exception of Germany, where in any case the collapse of the mark renders comparison difficult.

The secret of cheap oxygen is large liquid air units worked to their full capacity. By having increased the size of our factory units since the war we are able now to sell oxygen below our pre-war price. The oxygen business has become a good barometer of trade. It has suffered severely during the prolonged industrial depression, but the demand has been perceptibly increasing within the last two months. If this continues, as everybody must hope will be the case—for it will indicate improved general conditions in trade—then it will be obvious, from the figures I have given, that with an increased output still further reductions in the price of oxygen in cylinders should become possible.

The amount of oxygen sold in this country for medical purposes of every kind probably does not exceed 1 per cent. of the total output in cylinders. About 3 per cent. is used for limelight and experimental purposes. All the rest goes to industry. Of the industrial uses for compressed oxygen the most important is now metal cutting. This must represent over 50 per cent. of the total demand, and is about equally divided between scrap-cutting, or destructive work, and much important constructive work. The latter is perhaps one of the most promising outlets for oxygen. When the oxygen cutter is employed in conjunction with self-feeding profiling machines, now constantly being designed for various classes of work, it is found to operate almost with the precision of a saw and with far greater rapidity. Oxy-acetylene welding ranks next to metal cutting amongst the industrial applications of oxygen. About 25 per cent. of the gas sold in cylinders is employed for that purpose and it is becoming obvious that oxy-acetylene welding can easily hold its own in a great variety of work against electric welding and other processes. The remainder of the oxygen sold in cylinders is mostly employed for lead burning purposes and for obtaining high temperatures in special metallurgical operations.

In the wider fields of industry where the use of oxygen has often been suggested, as for instance in the enrichment of air for blast furnaces, and in conjunction with steam, for the continuous gasification of fuel, it is doubtful whether the stage has yet been reached when oxygen can be produced cheaply enough even in large plant units to be economically employed. In Germany oxygen is used in the manufacture of nitric acid and acetic acid, but otherwise neither in that country nor any other, so far as I am aware, has the use of oxygen yet developed to any appreciable extent in the chemical industry.

It must be admitted that industrial development throughout the world is still mainly confined to the cylinder trade. In this country, in spite of trade depression, the quantity of oxygen distributed in cylinders at the present time must approach 300 million cubic feet per annum (of which upwards of 225 million are supplied by the British Oxygen Company). In France I believe the annual output is about the same as here, but it is stated to be three times as much in the United States of America and more than twice as much in Germany.

At the outset of this paper I expressed the intention of limiting myself to an interpretation of its title which would permit me to deal exclusively with the separation of the constituents of the air. I wish, however, to explain that I had not advanced far with my subject before I realised that I should have to limit myself still further and abandon the consideration of all constituents except oxygen if I attempted any historical review of the industrial production and use of that gas. I have therefore confined myself to the subject on which I am best informed and have devoted this paper exclusively to oxygen. I offer no apology for this because I believe that the industrial importance of oxygen to-day warrants independent consideration.

During the war the supply of oxygen was described by a prominent member of the present Government as a matter of paramount national importance. This was certainly no exaggeration at that time and since the war the economic value of oxygen in the industrial applications I have mentioned, has been recognised to the full. Unfortunately exaggerated claims and statements are very apt to breed misconceptions in these difficult days of abnormal exchanges and keen international competition. I am therefore grateful to this important society for affording me an opportunity of placing on record what I believe to be a reliable statement of the present position in the oxygen industry.

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# THE MANUFACTURE OF HYDROGEN BY THE PARTIAL LIQUEFACTION OF WATER GAS AND COKE-OVEN GAS.

By Georges Claude, of Paris.

(Translated by H. Borns.)

For a number of years I have been engaged in the manufacture of hydrogen by the partial and direct liquefaction of water gas and its analogues. For this purpose water gas, compressed to a suitable degree, is in the first instance deprived of its carbon dioxide and is dried. The gas is then sent into a heat exchanger E, Fig. 1, in which it is cooled by circulating in the opposite direction to the hydrogen and carbon monoxide which have already been separated. The gas then enters by the collector C the bottom of a sheaf of vertical tubes F, the lower portion of which plunges into a bath of carbon monoxide boiling under atmospheric pressure. By the combined influences of the pressure and of the temperature of the liquid bath a large portion of the carbon monoxide of the ascending gases is liquefied; it flows back into the collector C. Owing to the pressure this liquid is forced out through the tube T and the cock R into the vaporiser V, where it replaces the liquid which is being evaporated. The remaining gas, containing hydrogen and a little of the residual CO, continues to rise in the sheaf of tubes F. There the gases encounter a temperature which is being more and more lowered by means which I shall presently explain. Under that influence the rest of the carbon monoxide is liquefied. *Theoretically*, therefore, it is a sensibly pure hydrogen which escapes from the top of the tubes, and it is this cold and compressed hydrogen which is expanded in the nozzle D and further cooled by this expansion to be sent back around the sheaf F, in order there to produce the very low temperatures of which I have just spoken.

In working this process two sources of inconvenience were experienced which I have only recently been able to overcome. In the first instance, when the hydrogen is entering the expansion engine at extremely low temperature as indicated, the frigorific efficiency of the expansion will be very low. There is in that case a progressive loss of liquid, unless we go up to pressures unduly high from the point of view of energy expenditure, and this all the more so because none of the customary lubricants can be employed at temperatures below – 200° C. Hence there is abnormal friction in the engine which will again lower the frigorific efficiency. In the second instance, the calorific mass of the gases, leaving the tubes and afterwards the nozzle D and circulating about the rising gases, will be smaller than that of the latter by the whole mass of the carbon monoxide which had been liquified by their action. As a consequence the ascending gas cannot, even assuming a perfect heat exchange to take place, leave the sheaf of tubes at the temperature at which the expanded gases entered the tubes. The final temperature of the expansion of the hydrogen will, therefore, not be very low, and in addition this temperature will be badly utilised for the purification of the ascending gases.

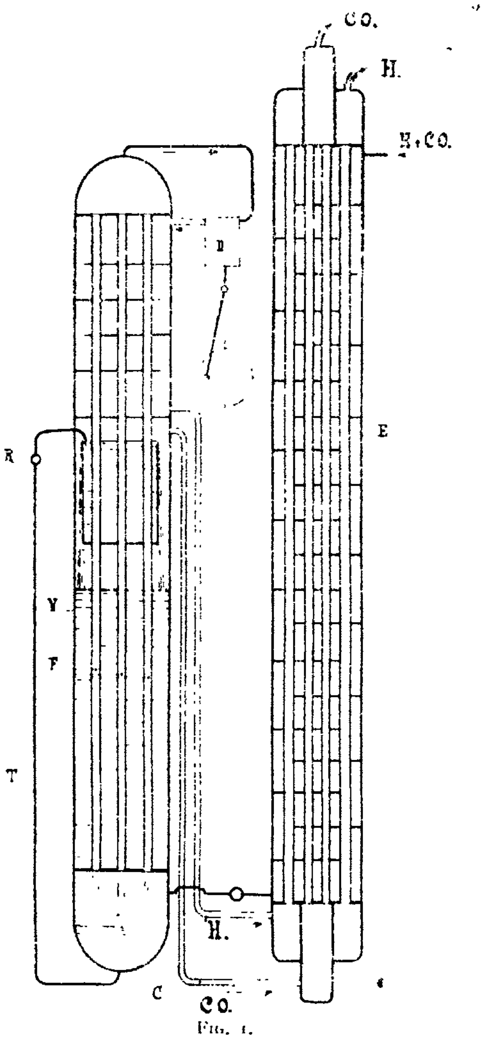

FIG. 1.

These various troubles have been overcome in the following manner:—

1. Part of the compressed gas which is entering the system is withdrawn from the heat exchanger E at a point M, Fig. 2, before it arrives in the cold portion; it is thus relatively little cooled. It is sent through the tube *t* into an auxiliary system of tubes G around which the hydrogen, leaving the bundle and passing on to the nozzle, is being circulated by

means of the pipes L and K. This relatively warm gas will then reheat the hydrogen before its expansion and will hence increase the efficiency of the expansion process.

2. If we relied exclusively upon this means, the final temperature of the expansion would remain unsatisfactory owing to the want of lubrication and to the eventual freezing out of the residual CO (– 206° C.). We must manage to lubricate the machinery by a substance which will remain liquid when the temperature sinks below – 206°. That body cannot be petrol ether, nor any similar substance since they would all be solidified at this temperature. I have, therefore, made use of nitrogen which only solidifies at – 211°

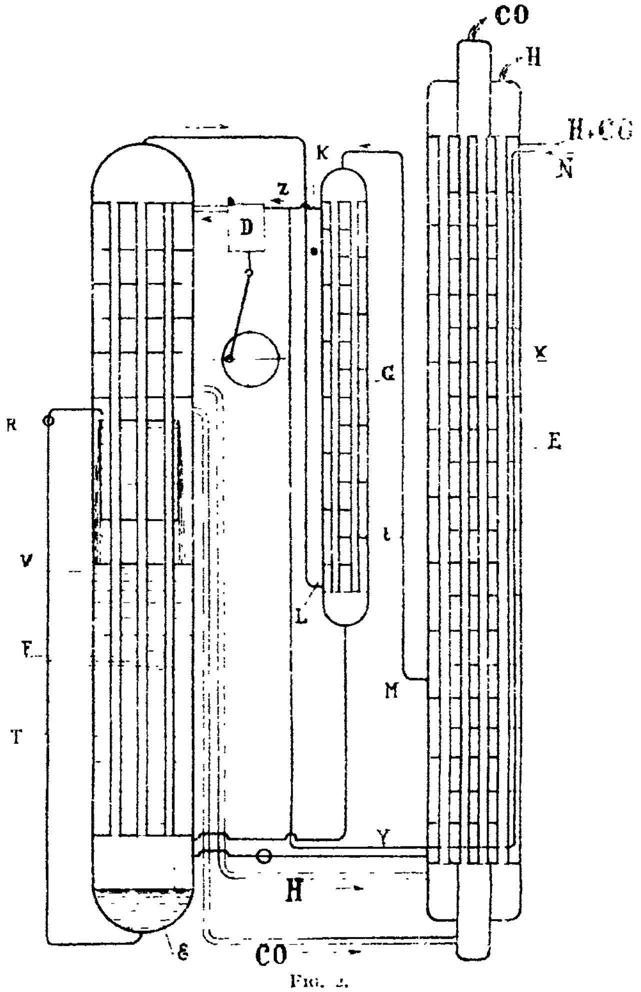

Fig. 2.

and which can moreover be added to the hydrogen, before its expansion, without causing any complication, at least in cases when we are aiming at the synthesis of ammonia. A current of compressed and dried nitrogen is cooled down to about its condensation point in the heat-exchanger E by means of the tube system XY; it is then added to the hydrogen at Z, before the hydrogen enters into the nozzle. In this way then we secure acceptable conditions for the lubrication. As a first consequence the temperature of the escaping gas is easily lowered down to − 208° and − 210° C., as soon as we lubricate by means of nitrogen. As a second consequence this addition of nitrogen to the gases leaving the tubular system increases, to any extent that we desire, the calorific mass of the expanded gas. The latter gas may therefore equal or surpass in mass that of the gas ascending in the sheaf F, including the carbon monoxide which has been condensed in this part of the tubes. As a result the temperature of expansion is considerably improved, and it is moreover much better utilised. We can indeed easily eliminate by these means the carbon monoxide within 1 per cent., and the hydrogen finally isolated can without any difficulty be used in my *hypercompression* process for the synthesis of ammonia.

This process has been developed and put into practice in the works of the Grande Paroisse, near Montereau, where an apparatus for the production of 500 $m^3$ of hydrogen per hour is in operation, feeding a unit for 5 tons of ammonia per day. The carbon monoxide, containing all the nitrogen of the water gas it should be noted, is discharged at a percentage which may easily be raised to 85. The amount of pure hydrogen obtained by this method is therefore very satisfactory. The carbon monoxide may be utilised, either for the manufacture of various chemical products, or for driving the internal combustion motors of the installation. The latter utilisation has been adopted in Montereau.

The process which I have outlined requires the compression of the gases to degrees, varying with the size of the apparatus from 15 to 30 atmospheres. The first figure applies to apparatus of a capacity of 2000 $m^3$ of hydrogen per hour. This process necessitates the command of a relatively high motive power, and one may draw attention to the advantages offered by processes based upon the catalysis of $CO$ into $CO_2$, such as are employed in the Haber process. I have therefore only studied and tried this process with a view of its ultimate application to a particularly interesting case, that of the *coke-oven furnaces* (and also that of town gas) in which the presence of a considerable portion of methane renders catalytic processes inoperative. The complexity of the gas mixtures we have to deal with in this case and the diversity of the freezing points of the constituents may make us fear that we should have to meet serious difficulties in the working of this process. As a matter of fact, however, an apparatus has already been constructed for this purpose and it has, after very short trials, been put successfully to service in the Béthune mines. The essential cause of the success is the very high reciprocal solubility of the diverse condensable constituents. This first apparatus has a productive capacity of 350 $m^3$ of hydrogen per hour, and it is operating with a compression of about 27 atmospheres. An installation for the utilisation of the hydrogen produced by means of this apparatus in the manufacture of ammonia by the application of hypercompression has already been erected and is actually being put in working order. I hope that this installation will be the point of departure for a much more important installation in which I intend to make use of apparatus for the production of 2000 $m^3$ of hydrogen per hour.

One of the essential reasons that make me count upon a development of this process in the coke-oven industry lies in the many indirect advantages which the process promises.

On the one hand, since the gases to be treated must already be compressed for the extraction of the hydrogen, we are naturally led to effect the stripping of the gas of its benzol likewise under pressure. All the benzol which at present escapes when the process is carried out at atmospheric pressures, will then easily be retained: that will constitute a gain which in certain cases may come up to 1 kilogram of benzol per ton of coke. This improved recovery will moreover be attained by means of a greatly reduced amount of solvent and of heat energy, and at much diminished losses of solvent. The recovery will be effected in absorption and distillation apparatus of comparatively very small dimensions. On the other hand the ethylene, this precious gas, the percentage of which in furnace gases is too low for its extraction with much success at atmospheric pressure, may easily be collected to a large extent in the course of the operations. For it will be condensed almost alone in the preliminary cold-exchanger of the apparatus, and it can be extracted as a 40 or 50 per cent. mixture which will very readily be utilisable, either for the manufacture of alcohol or for use in autogeneous welding or similar uses. To give an idea of the possible importance of this by-product I may state that, supposing the furnace-gas treated to contain 1·5 per cent. of ethylene and that it can all be extracted, this would correspond to our obtaining 200 litres of alcohol per ton of ammonia in addition to other products.

Finally I should remark that from the calorific standpoint hydrogen must be regarded as the very worst of all combustible gases. One cubic metre of hydrogen represents only about 2600 calories (lower calorific power) against the 3000 calories of carbon monoxide and the 10,000 of methane. When therefore we extract the hydrogen from coke-oven gases we, in fact, enrich the gases in a true sense, and it is a considerable enrichment which they undergo, since they become fit for uses for which they would otherwise be unsuitable. When the gas is to be distributed it will be completely free of every trace of the condensable impurities that cause so much mischief in our actual gas distribution systems; when it is to be utilised as industrial gas, it will enable us to obtain extremely high temperatures and to combine, for instance, under specially interesting conditions, the production of nitric oxide by the Hausser process with the synthesis of ammonia.

These are the principal advantages of the process which I have the honour to describe before you. I should like to emphasise that one of the characteristic essential features of the process is the extreme smallness of the necessary apparatus. An apparatus for 1000 $m^3$ of hydrogen per hour requires a sheaf of liquefaction tubes, 40 cm. in diameter and 3 m. in height.

# THE PRODUCTION OF LIQUID OXYGEN FOR USE ON AIRCRAFT.

By Edgar A. Griffiths.

## PART I.

### Storage and Transport of Liquid Oxygen.

- Introduction.
- Containers insulated with materials of low thermal conductivity.
- Vacuum insulated containers.
- Glass and porcelain containers.
- Metal containers.
- Absorbent material for removing residual gases.
    - (*a*) Charcoal
    - (*b*) Silica gel.
- Precautions to be observed in exhausting the interspace
- Rate of loss from commercial vessels.
- Separation of the thermal leakage into its components.
    - (*a*) Conduction down the neck.
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    - (*c*) Radiation transfer between the walls.
    - (*d*) Use of a radiation shield.
- Methods of generating gas from the liquid as desired.
    - (*a*) Heylandt's Vaporiser.
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## PART II.

### Production of Liquid Oxygen.

- Description of laboratory plant.
- Liquid oxygen plant with expansion engine.
- Portable Claude type oxygen plant.

## Part I. Storage and Transport of Liquid Oxygen.

### *Introduction.*

The atmosphere is so attenuated at the altitudes at which flying must be carried out for certain military purposes that the human lungs are unable to obtain the requisite amount of oxygen for normal respiration. The quantity of oxygen absorbed per minute is about 3 to 4 litres out of a total volume of 60 litres of air measured at normal temperature and pressure. The weight of air passed through the lungs at 20,000 feet is reduced to half and therefore needs to be considerably enriched in oxygen. Oxygen apparatus must supply about 4 normal litres of gas at these heights for comfort and safety. The oxygen in the early days was carried in cylinders under pressure, but the weight of such cylinders[1] is considerable, and a reducing valve is also required.

If liquid oxygen is substituted for high pressure gas the liquified gas is equivalent to compressed gas at 12,000 lbs. per sq. inch as against the 1800 lbs. which is the highest pressure that can be conveniently used in cylinders.

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[1] See Report of Gas Cylinders Committee, 1921.

The fundamental difficulty attendant upon the use of any liquified gas whose critical temperature is much below normal atmospheric temperature, is the maintenance of the containing vessel cold enough to store the liquid during transport and use. Thermal leakage must usually be paid for by evaporation of the liquid, and the evolved gas cannot, in general, be utilised. The employment of the liquid gases may therefore become very inefficient, unless due care is taken in selecting a proper container.

In dealing with liquid oxygen, for example, a temperature of $-185^{\circ}$ C. must be maintained and as the latent heat of oxygen is only about 50 gram-calories a litre will be evaporated for every 72 calories of heat that leaks in. This quantity of heat is roughly equivalent to the conduction into the vessel by a 1 cm. length of copper wire 0·004 sq. cms. in area in one minute for a temperature difference of about 200° C. between its ends. The heat required to raise the gas from its boiling point to the temperature at the exit from the neck is not usually obtained from the spherical portion of the vessel, but this heat absorption influences the conduction along the neck only.

For the high order of insulation necessary in the storage of liquid air and oxygen, two classes of containers have been used; firstly, vessels insulated with layers of material of low conductivity, secondly, double-walled containers evacuated to provide a vacuum space around the inner vessel.

(*a*) *Containers Insulated with Materials of Low Thermal Conductivity.*—For ordinary size vessels the use of the first method is practically out of the question since the materials available have for the thermal conductivity at low temperature a value not appreciably different from that at room temperature, and the heat conduction through a moderate thickness is usually very considerable. For instance, an experimental vessel was made holding 60 lbs. of liquid oxygen with a thickness of 3 inches of magnesia; this vessel evaporated the contents in one day.

The robust nature of this type of vessel would make it admirable for transport, but it is also open to several objections, namely :—

1. It is very difficult to maintain the insulation dry, in view of the unavoidable condensation of dew over the exterior surface, and a state of dryness is vital to the efficiency of the insulation.
2. The vessels are bulky and heavy.
3. They evaporate a very considerable amount of liquid in the cooling down of the insulation.

In the case of vessels in constant use for storage purposes, the last objection would hardly apply.

Insulated vessels, resembling "Thermos" flasks, are made commercially for household use. They have welded steel inner and outer shells with the interspace packed with a form of natural graphite, and partially evacuated. Such vessels are of but little use as liquid air containers, since the rate of loss is of the order of 340 grams per hour for a 4½ litre capacity vessel, and slightly less for a 2 litre capacity vessel.

This rate implies total evaporation of the liquid in about 16 hours.

It may be remarked that the high rate is partly due to the short neck and its large diameter.

(*b*) *Vacuum Insulated Containers.*—The alternative type of vessel to the lagged container, and the only practicable one at present, is the vacuum-walled container. Such vessels are made both of metal and of non-metals such as glass, quartz, and porcelain.

(*c*) *Glass and Porcelain Containers.*—The advantage possessed by glass and similar materials for the construction is that the vessels can be made seamless and heated to a high temperature to free the walls of

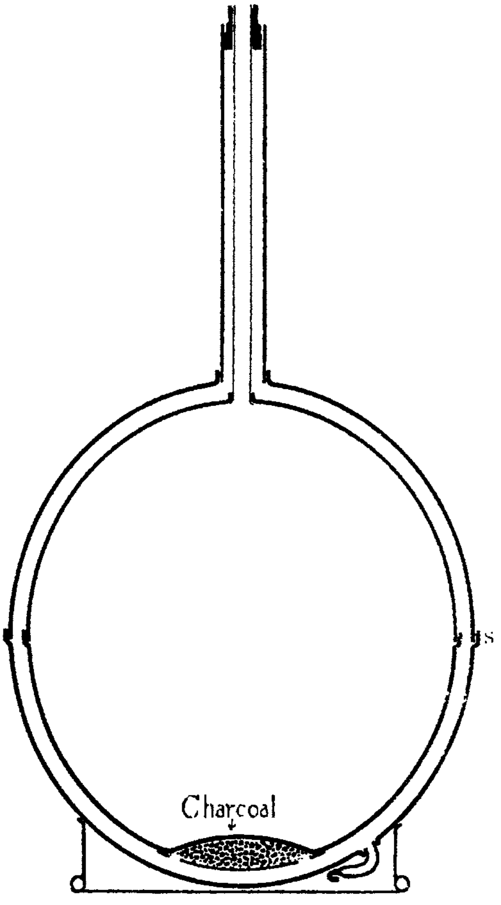

FIG. 1.—Metal vacuum walled vessel with charcoal pad.

gas during evacuation. Hence no absorbent material is necessary in the interspace to remove residual gas.

The efficiency of the glass type of vessel varies very considerably with different vessels, due presumably to variations in the degree of evacuation. In our experience, a half-litre vessel would be classed as good if its rate was only of the order of 110 grams of liquid oxygen evaporated per day: the corresponding figure for a litre vessel being 230 grams.

Of course a vessel will often show a rate many times this value and then re-evacuation produces a considerable improvement.

Glass vessels with a capacity of 5 litres (one gallon) have been made, but their fragility renders them of little use outside the laboratory. In any case it is necessary to syphon the liquid out of the large sized vessels as the stress on the necks becomes excessive when an attempt is made to pour out the liquid.

Large vessels are very difficult to construct.

Efforts have been directed towards the development of porcelain vacuum vessels of large size, since experiment indicated that this material was suitable for the purpose. However, the quantity production of such vessels has not been proceeded with, as the metal flasks show many advantages.

In Germany porcelain vessels were manufactured of large size and used for the transport of liquid oxygen, but the manufactured now seems to have been abandoned.

(*d*) *Metal Containers.*—Metal vacuum vessels are now constructed commercially in various sizes, the usual form is shown in Fig. 1. The inner and outer shells are made up of hemispherical spinnings soldered together along circumferential seams. These seams are marked *s* in Fig. 1, and are made by the use of a blow-pipe, each joint being previously tinned. Care is necessary in the use of flux as spirits are apt to penetrate into the inner space and dull the polish, even rosin leaves a decided atmosphere in the flask. The bottom of the inner neck is flared out to carry the weight and also well soldered as it is here that fracture generally occurs. The top of the neck is finished with a brass collar which is grooved to receive the solder which is well melted in.

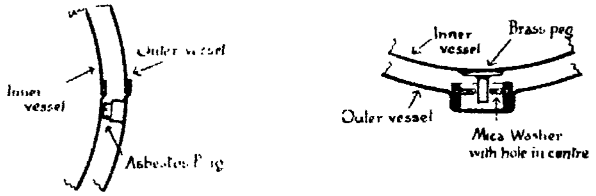

FIG. 2.—Two methods of supporting inner vessel concentric with outer vessel.

The inner neck is the only metallic contact between the two vessels and its conductivity is therefore important; for this reason the material should be as thin as possible and about 1 cm. in diameter.

In practice tubing less than about 20 S.W.G. is difficult to obtain, the metal is inclined to develop flaws in manufacture.

In large vessels some additional support is desirable for the inner vessel especially to prevent the inner vessel swinging about and breaking the neck. This may be prevented by a number of small asbestos blocks around the circumference, or any other insulator may be used which is capable of withstanding heating to about 100° C. during evacuation without decomposition.

An alternative method is also shown in Fig. 2, where the inner vessel is provided with a projecting pin which fits into a hole in a mica washer held in a tube fixed to the outer vessel. This method has been found very satisfactory in practice.

## *Absorbent Material for Removing Residual Gases.*

All commercial vacuum vessels now in use have a quantity of absorbent material in the vacuum space which clears up the residual gas when cooled down by the filling of the vessel. Metal vessels can be made without an absorbent,[1] provided they are heated to at least 300 C. to free the walls from gas. Unfortunately the seams will not stand this heating unless hard soldered or welded, and the high temperature required for either of these processes dulls the polish on the walls and thus causes excessive radiation of heat. A very much lower degree of evacuation is required for a vessel containing an absorbent and in fact a Fleuss pump in good condition and dry will serve for evacuation.

(*a*) *Charcoal.*—The best absorbent, according to Dewar,[2] is charcoal made from shells or fruit stones, but almost any variety can be used; even coal absorbs a considerable amount of gas. The quantity of good charcoal required is very small and 4 grams for a volume of 100 c.c. interspace is ample.

The inflammability of charcoal is a matter for serious consideration in warfare and its use should be avoided. Non-inflammable substances such as silica gel serve the same purpose.

(*b*) *Silica Gel.*—This substance is well known as an absorbent and Professor Henry Briggs, on behalf of the Oxygen Research Committee (Department of Scientific and Industrial Research), has made a thorough investigation of its properties, especially with regard to low temperature applications in vacuum vessels. Silica gel has only about half the absorbing power of the best charcoal and it is also of lower density so that, when it is used in vessels constructed for charcoal, greater care is necessary in evacuation to ensure that the pressure is low enough not to leave too much air to be absorbed.[3]

## *Precautions to be Observed in Exhausting the Interspace.*

In charcoal absorbent vessels the evacuation is usually of quite a low order, and several vessels have been found to have as much as 1 mm. of mercury gas pressure in the vacuum space at ordinary temperatures and have yet remained serviceable. The chief objection to this high pressure is the prolonged interval required by the charcoal to absorb all the air when the vessel is filled. This may take as long as half an hour.

In evacuating vessels by any method a fundamental point is heating the charcoal to redness immediately before inserting into the vessel, and also heating the entire vessel to as high a temperature as the seams will stand, which is usually about 100 C., and maintaining at this temperature until the vacuum ceases to fall off when the pump is stopped for a few moments.

The chief object of this heating is to remove moisture.

## *Rate of Loss from Commercial Vessels.*

The rate of evaporation of liquid oxygen from good commercial vessels is of the following order of magnitude:—

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[1] *Annal. de Physique*, 1918.

[2] *Proceedings of the Royal Institution*, 1906.

[3] *Proc. R. S.*, Edinburgh, 1920-1.

| Capacity in Litres Liquid.[1] | Rate in Grams per Day. | Percentage per Day. |
|---|---|---|
| 1 | 840 | 70 |
| 3 | 540 | 15 |
| 5 | 600 | 11 |
| 24 | 1290 | 4·5 |

The above values are averages relating to a large number of both German and English vessels that have been studied by the writer. A good glass vessel is therefore nearly twice as efficient as a metal vessel, but the average vessel, especially such as used for household purposes, is quite the reverse.

### *Separation of the Thermal Leakage into its Components.*

The sources of loss in a metal vessel can be divided into three classes, i, conduction down the neck tube, ii, gas conduction across the interspace, and iii, radiation between the two walls.

The percentage rate is rate of loss calculated for a full vessel: the percentage calculated on the actual contents increases uniformly as the vessel empties since the rate of evaporation does not fall off as the volume of liquid decreases.

(*a*) *Conduction down the Neck.*—The magnitude of the heat leakage into the flask by conduction along the neck depends upon the length of the neck, its cross-sectional area, and the thermal conductivity of the material. Manganin with the low thermal conductivity of 0·035 C.G.S. units is a suitable material for the construction of the neck, but thin-walled tubes of this material are difficult to obtain. The nearest approach to manganin is German silver which is extensively used in Germany for the purpose, but it is difficult to obtain tubes in this country. The only alloy readily obtainable is copper nickel (German silver without zinc). This is of distinctly higher conductivity and is moreover liable to the development of flaws in manufacture. For practical reasons connected with filling it is undesirable to use tubes smaller than 1 cm. bore and they should preferably be $1\frac{1}{2}$ cms. The thickness of wall is generally of the order of 0·8 to 1 mm. so that the area of metal is about 24 to 45 sq. mm.

Some years ago it was pointed out by Swan in connection with Regnault's work on the specific heat of gases that the conduction of heat along a tube is influenced by the flow of gas in the tube, and that this is a factor to be considered in calculating heat leakage has also been pointed out by Professor Briggs. It is not therefore sufficient to assume that the two end temperatures determine the thermal transfer, but the actual gradient at the junction of the neck with the inner vessel must be considered.

The temperature distribution along the neck of a flask containing liquid oxygen is shown in Fig. 3. It may be remarked that the gas-temperature distribution has already been published. The temperatures shown are actual neck temperatures obtained by means of a fine thermocouple in contact with the metal wall and not the distribution of temperature along the gas stream. The E.M.F. generated by the copper-constantan thermocouple was measured by a potentiometer and the necessary precautions taken. The upper curve refers to an alloy tube and the lower to a brass tube of fairly high conductivity selected for contrast. The gas flow was about three-quarters of a litre in each case. In all the flasks tested a gradient of temperature was evident at the bottom of the neck.

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[1] The evaporation from the one litre size is unduly high, but very few of these have been made and no doubt they are capable of considerable improvement.

(*b*) *Conduction through Residual Gas.*—The second factor in the efficiency of the vessel, gas conduction, depends on the nature of the residual gas, the pressure and the area of the vessel. The gas present is mostly air with probably water vapour and hydrogen in small quantities. No direct determination of the pressure appear to have been published, but Dewar and Briggs have investigated the pressure indirectly by submitting a flask to various external temperatures and calculating the losses from assumptions based upon the fact that the

$$\text{total loss} = a(T^4_1 - T^4_2) + b(T^4_1 - T^4_2)\ \sqrt{T_1 + T_2}$$
$$+ \text{constant loss for neck,}$$

where $T_1$ and $T_2$ are the temperature of the inner and outer walls.

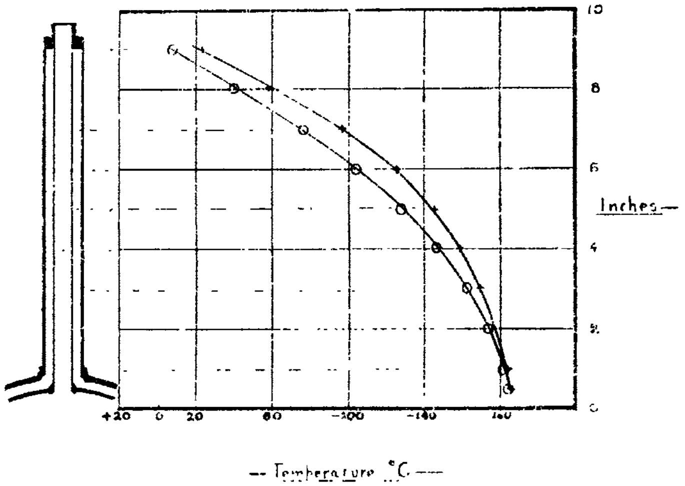


FIG. 3.

Curves showing distribution of temperature along inner tube of neck. Top curve alloy, bottom brass.

The temperature gradient depends upon the rate of flow of the gas out through the neck.

The first term refers to radiation transfer, the second to conduction.

For a metal flask Briggs found that the conduction was approximately equal to the neck loss at room temperature, and each constituted 25 per cent. of the total. These experiments were carried out with great care on flasks which are probably specially constructed and well evacuated, for the writer has found that the method when applied to commercial vessels passing through a cycle of temperatures changes gave the result shown in Fig. 4. In this case gas is evidently evolved from the walls even at moderate temperature elevations, and although the flask may have been heated during evacuation (the pressure is, of course, much lower when liquid oxygen is present in the flask than during evacuation period), the evaporation rate does not completely recover and return to its normal value for a considerable time. Hence the evolved gas is not readily absorbed by the charcoal;

the gas may be hydrogen in which case the value of the conductivity would be appreciably different from that of air.

The above method should therefore be applied with some caution except in the case of glass vessels.

(*c*) *Radiation Transfer between the Walls.*—The factor of greatest importance is the radiation transfer. The heat transferred by this means depends upon the emissivity of the walls and the fourth power of the absolute temperatures. The selection of the best reflecting surface for a long wave-length radiation at low temperature is still a matter for research as vacuum flask tests are of limited help in view of the many variables involved. Copper, gilding metal (a brass alloy), nickel and silver plating give much the same results within the limits of the order of accuracy of the experiments. Iron appears to be inferior, for it is difficult to obtain a high polish on it. The degree of polish of the walls is of considerable importance.

It is probable that little improvement is possible in the efficiency of the best metals without radical changes in design.

(*d*) *Use of a Radiation Shield.*—One promising line of investigation to

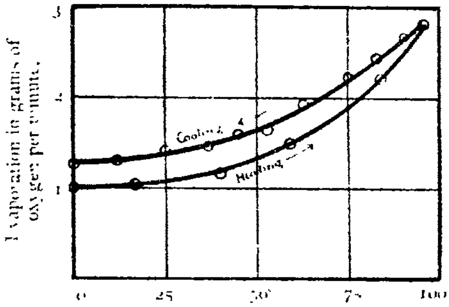


FIG. 4.—Effect of a cycle of temperature on the rate of a flask.

follow would be to effect a reduction in the radiation transfer by the use of radiation shields. The chances of improvement are greatest here as this effect is at present responsible for the largest loss.

It can be shown that the effect of reflecting surfaces is to reduce the radiation by $\frac{1}{n+1}$ where $n$ is the number of the intermediate surfaces, assuming that they touch neither wall. The writer has constructed one vessel with a radiation shield as shown in Fig. 5. The intermediate wall is supported from the neck by a thin steel tube which is slotted to diminish the cross-sectional area, but which yet provides a still support. This vessel has been used for transport purposes for about two years, and the efficiency is about 15 per cent. better than a vessel of the same size with two walls.

### *Methods of Generating Gas from the Liquid as Desired.*

When liquid oxygen is used as a substitute for compressed gas the liquid must be evaporated at a definite and steady rate to suit the requirements of the airman.

(*a*) *Heylandt's Vaporiser.*—The method devised by Heylandt is shown diagrammatically in Fig. 6.

The liquid is carried in a vacuum vessel and ejected by the pressure due to its natural evaporation and the stream passes up the neck through a small tube into a flask boiler where it is evaporated. The gas passes through a trap to catch any drops of liquid and thence through coils of copper pipe to the control valve which is graduated two, three, or five litres of gas per minute.

The pressure above the liquid in the container is shown by a small pressure gauge and regulated by a relief valve. The delivery of oxygen for any given setting of the valve depends upon several factors and varies from time to time for the same pressure reading.

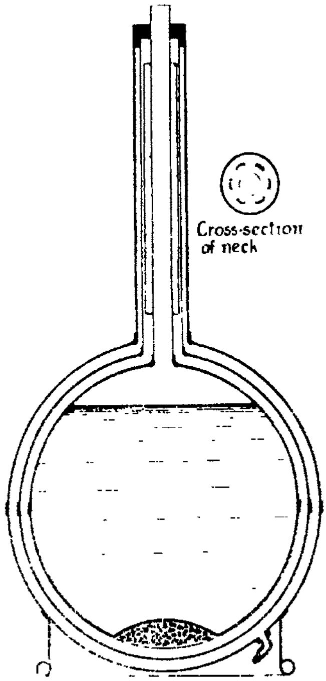


FIG. 5.
Metal vacuum vessel fitted with radiation shield.
This shield is carried from a tube attached to top of neck. The tube is slotted away to reduce heat conduction along it.

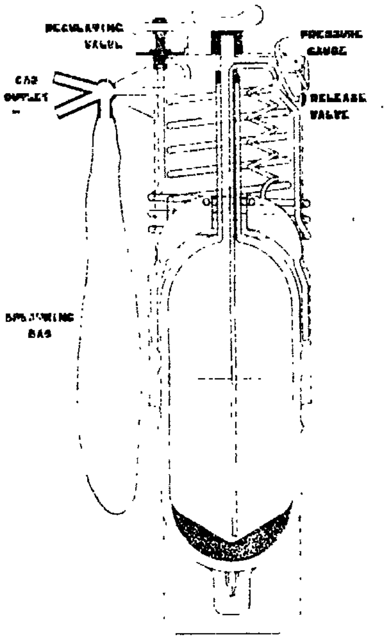


FIG. 6.

(b) *Griffiths' Vaporiser.*—The writer has also designed an alternative form of vaporiser as shown in Fig. 7, the action of which depends upon the varying metallic contact between the walls of the vessel. A copper pad is carried by a flexible diaphragm on the outer wall and adjusted into contact with the inner vessel by a screw. The evaporation can then be controlled with accuracy.

It is important that the diaphragm should be a good conductor such as silver or copper. The advantage of this form of vaporiser arises from the fact that the vessel may be non-spillable by absorbing the liquid into asbestos or similar material. A quantity of asbestos about 10 per cent. of the weight of the oxygen will suffice to absorb the liquid.

## PART II. PRODUCTION OF LIQUID OXYGEN.

The entire output of oxygen in this country, apart from a small medical demand, was in the early days of the war absorbed by the welding industry.

The only plants available for experimental work were small units of the form shown in Fig. 8.

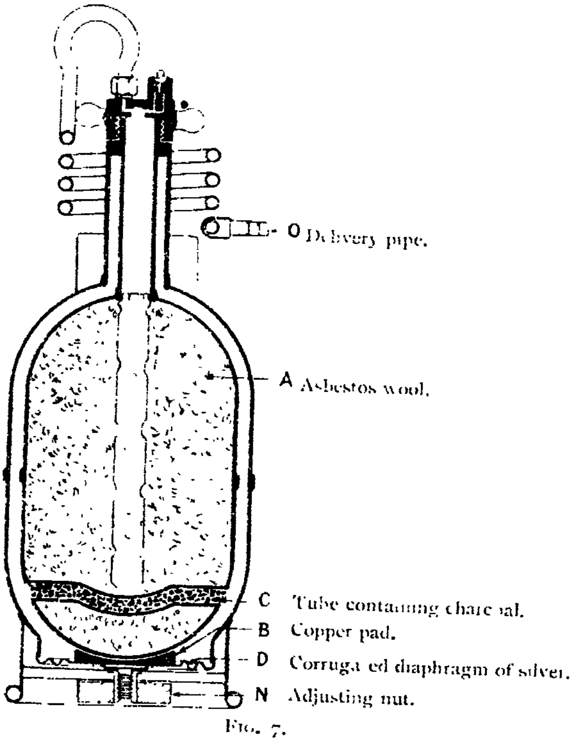


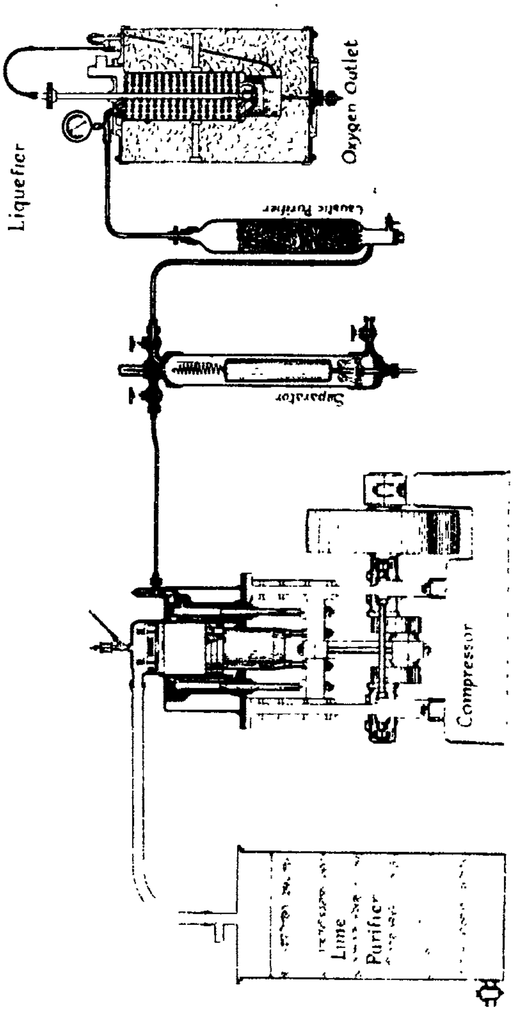
FIG. 7.

*Description of Laboratory Plant.*

The air is drawn in through a line of purifiers on the left, compressed to about 1,800 lbs. per sq. inch in a three-stage compressor and thence passing through a water separator and caustic potash column into a Hampson liquefier. The lubrication of the compressor is largely effected by water and the separator deals with this moisture. The liquefier consists of flat wound spirals of $\frac{1}{8}$ inch copper pipe; four tubes in parallel. At the bottom, these tubes merge into a valve which regulates the expansion. The output of these small plants is about one-third of a litre per horse-power hour of liquid air which must be rectified to obtain a high oxygen percentage.

The plant is fairly reliable if fitted with direct electric motor drive running at not more than 250 revolutions per minute, but chain, gear, or belt drive is troublesome on small compressors, since they are not generally provided with sufficently large flywheels.

The method of constructing the interchanger is open to improvement as caustic, if carried over, permanently chokes the tubes and the output suffers accordingly.



BRITISH OXYGEN LABORATORY PLANT.

FIG. 8.

It is well known that the Joule-Thomson effect employed by Linde gives a cooling effect of the order of a quarter of a degree per atmosphere, whereas the Claude system of making the air do external work gives a cooling effect $T_1 = 0{\cdot}29\, T_0 \frac{P_1}{P_0}$,

where $T_0$ = initial temperature
$T_1$ = final temperature
$P_0$ = final pressure (atmos.)
$P_1$ = pressure before expansion.

This leads to the conclusion that the cooling effect is about three times as great with the expansion engine; but in practice the expansion engine becomes very troublesome near the liquefaction point and the Joule-Thomson effect increases so that a combination of the two methods is usually employed. There is, however, very little difference in the performance in small plants with or without an expansion engine. but the outstanding feature which can be utilised is the fact that an expansion engine plant can be designed for about 40 to 50 atmospheres pressure at the compressor.

### *Liquid Oxygen Plant with Expansion Engine.*

To illustrate the general scheme of an expansion engine plant, one built by the Liquid Air and Rescue Syndicate will be described as it is the simplest, although it uses high compression. Air is drawn by the compressor, Fig. 9, through the scrubber in order to remove as much as possible of the carbon dioxide. The air enters the tower at the bottom. The absorbing agent (12 per cent. caustic soda solution) on the other hand flows from the top to the bottom through steel turnings and so meets the air and absorbs the $CO_2$. This purifier requires the circulation of the alkali by a pump which draws the liquid from the bottom and delivers it at the top. The air freed from $CO_2$ is drawn into the four stage compressor and compressed to about 200 atmospheres (3000 lbs. sq. inch). Between each stage is an intercooler. The air from the compressor passes through a water and oil separator to the high pressure drying bottle. Before entering the drying bottle the air passes through coils which are surrounded by the cold air leaving the liquefier and part of the water vapour is condensed. The remaining moisture is removed by the drying bottle.

The dry air passes to the liquefying plant which consists of a liquefier and an expansion engine. Part of the air passes through air-cooled coils on the outside of the liquefier and then enters the cylinder of the expansion engine in which it is expanded down to a low pressure, thus becoming cooled. This cold air passes through the separator and then enters the liquefier near the bottom by the pipe and rises through the heat interchanger. In this interchanger are many small pipes through which the other part of the compressed air passes downwards and gives up heat to the rising air from the expansion engine until this air finally reaches the expansion valve, cold but at high pressure. The air is expanded through the expansion valve to about atmospheric pressure and is thus further cooled. The cold air mixes with the expansion engine exhaust and helps to cool still further the incoming high pressure air.

By this means the air reaches the expansion valve at a continuously reduced temperature until part of it is liquefied on expansion. The liquid formed collects at the bottom of the liquefier and can be drawn off by a cock. The enrichment of the air in oxygen depends on the different boiling-points of the oxygen and nitrogen. The rectification column is situated at the bottom of the apparatus. The up-going gas meets the liquid flowing downwards and a gradual interchange takes place, the lower boiling-point nitrogen passing away as gas and oxygen liquid collect in the bottom. The purity of this liquid is about 75 per cent. The air leaving the interchanger passes through coils which cool the air passing to the expansion engine.

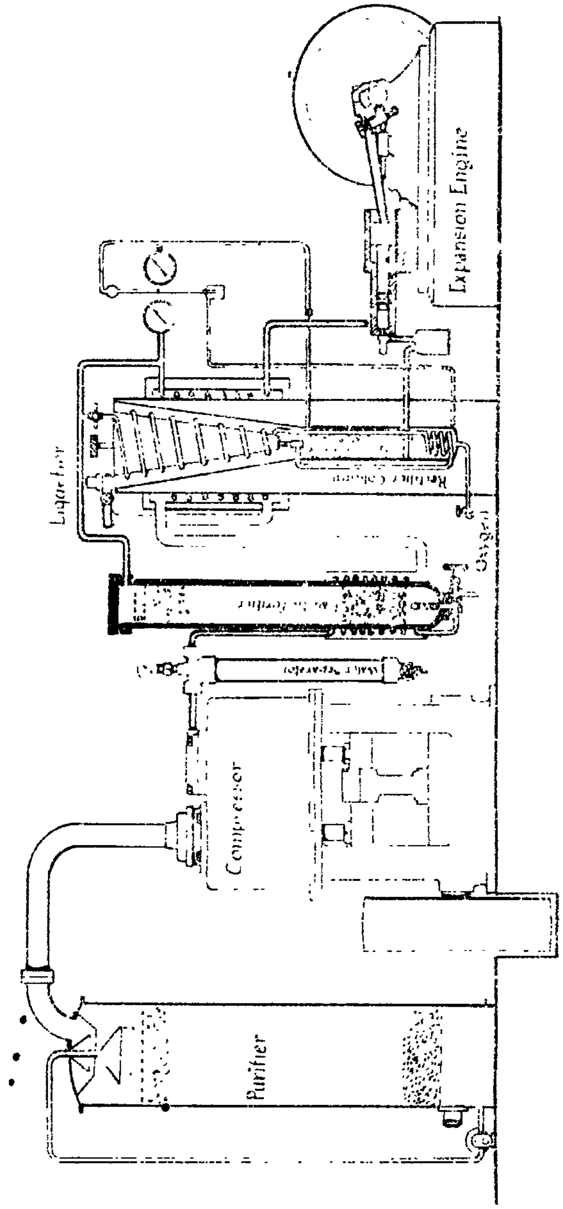


FIG. 9.—Liquid oxygen plant with expansion engine.

*Portable Claude Type Oxygen Plant.*

A plant using the Claude system is more elaborate. One made by Société L'Air Liquide Boulogne-sur-Seine, Paris, is carried normally on a railway truck. The general arrangement is shown diagrammatically in Fig. 10.

The air is compressed in a two stage compressor A and delivered at a pressure of about 15 atmospheres to the separator B where moisture absorbed from the injection water in the cylinders of the compressor is removed. The air then passes successively through the purifying chambers C (only one of which are shown), filled with caustic soda or caustic potash, and enters the liquefying column. The arrangement of the column and expansion engine are shown in Fig. 11. Air passes from the purifier by the pipe 1 into the temperature exchanger A, and traverses the nest of small

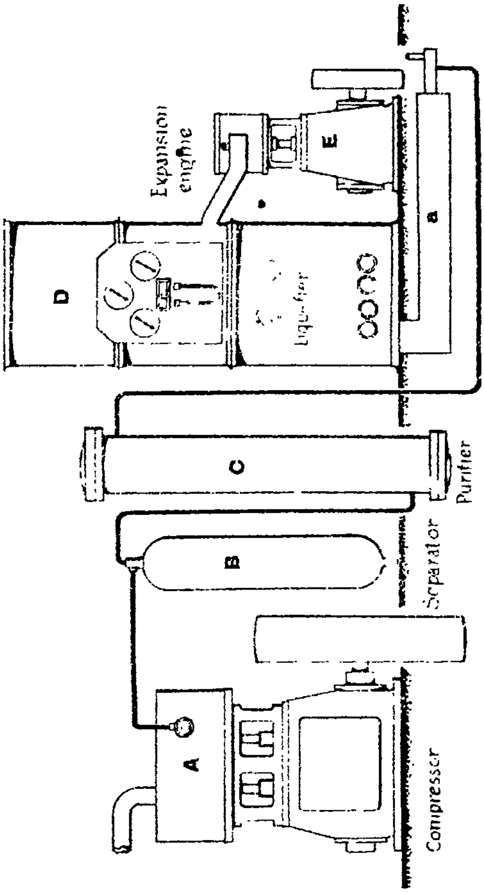


Fig. 10.

tubes 2 which are cooled by expanded and cold gas flowing in the opposite direction.

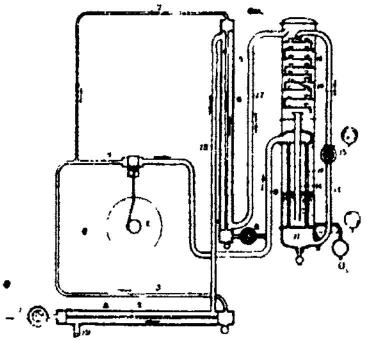


Fig. 11.—Diagram of liquefier on Claude system.

The cooled air leaves the temperature exchanger by the pipe 3 and part enters the expansion engine E, by the pipe 4, and the other part enters a nest of tubes 5 in the liquefier 6 by the pipe 10. The air entering the expansion engine does external work on the piston and is expanded and thus cooled. The compressed air in the nest of tubes in the liquefier is cooled by expanded and cold air flowing in the opposite direction and under the continued action of cooling and pressure liquefies, and passing through the needle valve 8, mixes in the pipe 9 with the cold air from the expansion engine. The cold air and liquid air enter the top of another nest of tubes 10 called the vapouriser, which is contained in the intermediate part of the rectification column. On leaving these tubes, the mixture of gas and liquid enters a sump 11 at the bottom of the column. From this sump it rises through the pipe 12 and regulating valve 13 to the top of the column. The top portion of the rectifying column contains a series of staggered and perforated trays 14 which are provided with caps 15. The liquid in the mixture descends through the trays and enters the vapouriser by means of the pipe 16 in the space surrounding the nest of tubes 10. The gas in the mixture, which contains a large quantity of nitrogen, since nitrogen has a lower boiling-point than oxygen, leaves the of the column by the pipe 17 and first enters the liquefier in the space

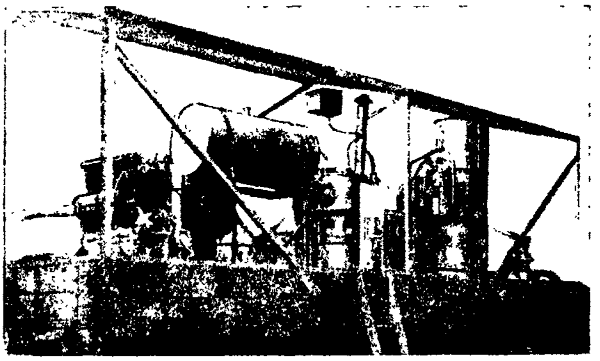


Fig. 12.—Portable liquid oxygen plant working on Claude system.

The expansion engine can be seen on the right, the column in the centre and the resistance frames for dissipating the energy developed in the dynamo attached to the expansion engine on the right. The air compressor is situated behind the resistance grid.

surrounding the nest of tubes 5, thus cooling the compressed air in the tubes. From there it enters the temperature exchanger by the pipe 18 in the space surrounding the nest of tubes 2, and fulfils the same function of cooling the compressed air flowing in the opposite direction. It leaves by the pipe 19, warmed but still at some degrees below the temperature of the incoming air.

When the liquid air supply is sufficiently large for liquid oxygen to be produced, the valve 13 is slowly closed down but not completely shut. The exhaust pressure in the expansion engine then rises to the same pressure as that of the liquid air in the nest of tubes 10 in the vapouriser and causes the surrounding liquid to boil. The gas thus formed rises through the plates 14 while the liquid formed passes through the valve 13 and flows into the top of the columns. The liquid descends through the trays while the gas bubbles around each of the caps.

The output of this plant is about 20 litres per hour of 96 per cent. purity oxygen. The horse-power by independent test of the compressor is slightly less than 60 or 3 H.P. per litre per hour.

A photograph of the complete plant is shown in Fig. 12. The expansion engine on the extreme right drives a dynamo, the output of which is absorbed by a variable resistance. About 3 electrical horse-power is produced in normal running.

This plant produces liquid in four hours, the average output being 43 lbs. per hour for each successive hour. The pressure at the compressor is 45 atmospheres at 250 R.P.M., and the expansion engine runs at 160 R.P.M., producing 2500 watts.

The purity of the liquid oxygen is 96 per cent.

# THE HEYLANDT LIQUID AIR PLANT.

By A. J. Bremner, B.Sc., A.M.I.Mech.E., Technical Manager of Liquid Air (Limited).

The development of the "Aerophor" Liquid Air Self-contained Breathing Apparatus by this Company, made the construction of comparatively small but efficient liquid air production plants a necessity. With this end in view co-operation followed with Heylandt of Berlin, for the purpose of improving upon existing systems, and this resulted in the Heylandt plants which represent a marked advance in industrial methods of air liquefaction generally and particularly in regard to economic production and simplicity of operation.

The first standardised plants were designed for an hourly output of 10 litres liquid air of 60 per cent. oxygen content (this being the quality required for mine rescue purposes), or up to 15 litres of liquid air per hour, but with a lower oxygen content.

The special feature of the Heylandt plants is the expansion engine, which takes the place of the refrigerating plants, and other pre-cooling devices commonly employed with other systems, and achieves the same end in a more simple and economical manner.

As is well known, when a gas is compressed the work of compression is converted into heat, with a consequent temperature rise, and conversely when a gas is expanded its internal heat is reconverted into work and its temperature falls.

The reasons why the process of expansion with external work had not previously been employed for obtaining low temperatures were not solely of a practical nature. Heylandt recognised that with a suitably constructed expansion engine the high cooling effects owing to the external work could only be attained with absolute safety of operation if the highly compressed air were expanded within a cylinder to practically ordinary pressure by a rapid expansion. The fall of temperature thus caused by a single expansion is about 160° C. whilst the moving parts of the expansion engine remain almost at ordinary temperature and can therefore operate on ordinary lubricating oil. This process which was developed between 1908 and 1910 was on account of the then prevailing views considered impracticable, but the large number of plants now operating most satisfactorily proves that Heylandt chose the correct means.

The cooling effect based on Heylandt's process, fairly accurately follows the formula:—

$$T_1 = T\left(\frac{p_1}{p}\right)^{\frac{k-1}{k}}.$$

($T_1$ = final temperature; T = initial temperature; $p_1$ = final pressure; $k$ = the ratio of the two specific heats.)

This effect starting with the same initial temperatures is more than double that obtained by Linde's formula :—

$$\delta^{\circ} = 0{\cdot}276\,(p_2 - p_1) \cdot \left(\frac{273}{T}\right)^2$$

$\delta$ = fall in temperature $(p_2 - p_1)$ = difference of pressure in atmospheres and T = absolute discharge temperature.

The efficiency of the liquefying apparatus is excellent if the process as explained above is employed. A small plant requires only about 1·25 KW. hours for 1 litre of liquid air, containing 85 per cent. of oxygen. This corresponds to a power absorption of 1·4 KW. hours per litre of liquid oxygen with a purity of 96 to 98 per cent., a great number of plants have proved in practice that these figures are correct.

The Heylandt expansion engine is a power engine, while other cooling vices require work and thus encumber the already unfavourable balance of the generation of cold. The process of the expansion engine requires no chemicals ; it employs part of the compressed air which would be available in any case even in plants without the expansion engine. The air cooled down in the expansion engine to − 130 to − 160° C. serves as a cooling agent for the other part of the compressed air and thus effects its intense cooling and liquefaction. The work of the apparatus is therefore not solely effected by means of the throttling expansion of the expansion valve, but it is considerably increased by the expansion due to external work of the expanded gases. The production of liquid air without external work varies between 0·3 to 0·4 litres per H.P. hour. This figure is, when employing our process in connection with external work, increased to about 0·7 litres per H.P. hour. The efficiency of liquefaction of our plants when the expansion engine is employed is about 20 per cent., *i.e.* from 100 cbm. of aspirated air about 20 litres of liquid are obtained, whereas the efficiency of

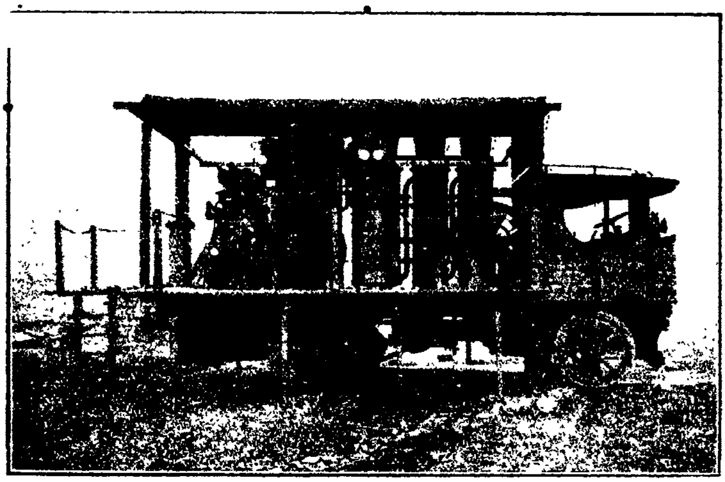


Fig. 1.

other systems is only 10 to 15 per cent. The effect of this is that by means of a compressor of only half the capacity the same output may be obtained as with other systems which means that the total cost of plant and liquid oxygen production are considerably decreased.

During the past eight years the Heylandt process has been extended, and a large number of plants employing this system are now operating for the production of gaseous oxygen in which the simplicity of operation and economic production remain the special features. In the plants designed for the production of gaseous oxygen the expansion engine still serves a valuable part, but in this case is only used for reducing the period required for the initial cooling down of the apparatus, as against its continuous use with the liquid air plant. The liquid air plants work at a pressure of 200 atmospheres, and the gaseous oxygen plants when on production operate at between 40 to 60 atmospheres pressure according to size.

The illustration shows a plant designed for the continuous production of 10 litres of liquid oxygen per hour, and the compactness of the apparatus will be appreciated from the fact that the whole of the plant including the power unit can be erected upon a five-ton steam lorry.

Heylandt liquid air plants are constructed with capacities ranging from 1 litre per hour upwards, and the gaseous oxygen plants with hourly output ranging from 70 to 3500 cubic feet, and examples of both are running at this Company's works.

# THERMOMETRIC LAG WITH ESPECIAL REFERENCE TO COLD STORAGE PRACTICE.

By Ezer Griffiths, D.Sc., and J. H. Awbery, B.A., B.Sc., National Physical Laboratory.

Temperature control is a factor of such vital importance to the successful operation of a cold store that the instruments employed should receive the most thorough study. Mercury in glass or spirit thermometers are almost universally used for such measurements and have the merit of extreme simplicity. For distant reading work the resistance and the mercury in steel thermometers have obvious advantages and are now finding applications.

The object of the experiments described below was to obtain numerical data as to the magnitude of some of the possible sources of error in the measurements when mercury or spirit thermometers are employed for taking the temperature of the atmosphere of a ship's hold by withdrawal of the thermometer to the deck for reading. They also give information as to the error introduced by the "time lag" of the thermometer if the temperature of the store happens to be changing rapidly.

Besides the spirit and mercury thermometers generally employed in such measurements, tests were made on a resistance thermometer and a distant reading mercury thermometer.

## Description of the Various Types of Thermometers.

A. *Mercury in Glass and Spirit Thermometers.*—The mercury thermometer shown in Fig. 1 was designed by Mr. A. R. T. Woods, Managing Director of the Nelson Line, with a view to eliminating a most serious source of error in the common type, namely, the rapid change in reading which occurs when a bare thermometer is withdrawn from the hold and read on deck. Mr. Woods states that this error was often accentuated by the observer holding the bulb in the palm of his hand when taking the reading.

In the form shown in Fig. 1 both the bulb and stem are protected by a wooden sheath, while the bulb is lagged by cotton waste. The efficiency of this simple device for overcoming this particular difficulty is demonstrated by the experimental data given later in this report.

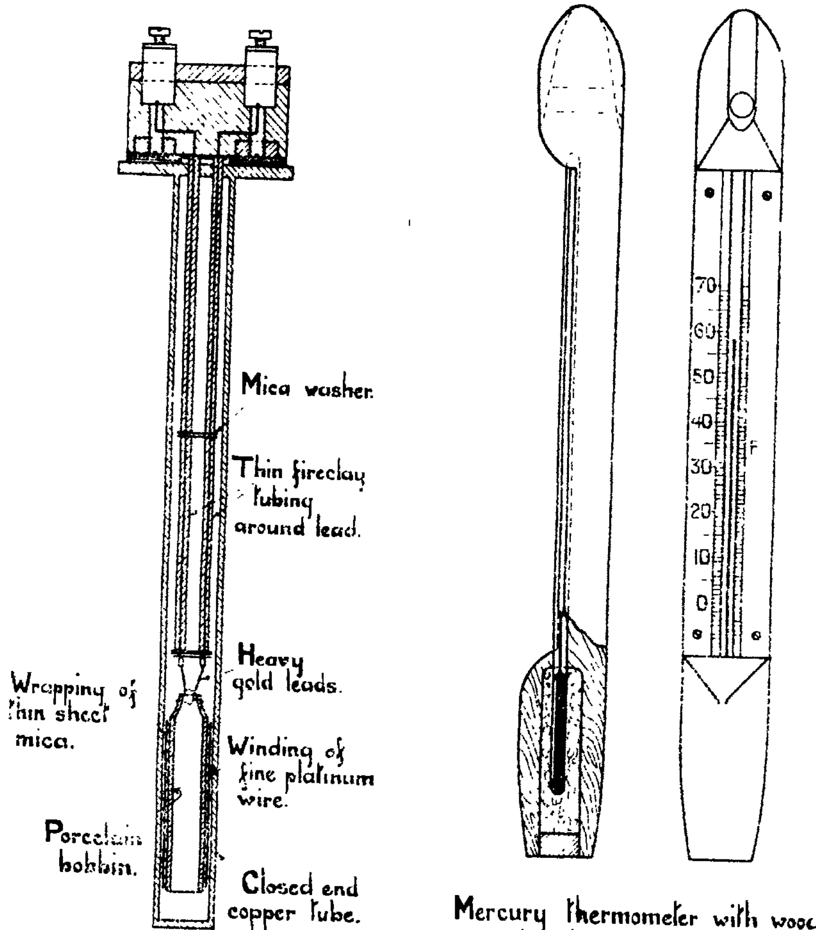
Plain mercury and spirit thermometers were also studied; the bulb of the former being $\frac{1}{4}$ inch in diameter and 1 inch long, of the latter $\frac{3}{8}$ inch in diameter and $1\frac{3}{8}$ inch long.

B. *Mercury in Steel Thermometer. Distant Reading Type.*—In this instrument the mercury is contained in a steel bulb, connected by a fine capillary to a Bourdon tube. The temperature is indicated on a dial resembling a steam pressure gauge. The bulb of the thermometer is cylindrical, $\frac{3}{4}$ inch in diameter and 8 inches in length.

C. *Resistance Thermometer.*—The "bulb" of this thermometer consisted of a porcelain spool $2\frac{3}{16}$ inches long by $\frac{7}{16}$ inches in diameter, wound with platinum wire, as shown in *Fig.* 1. After winding, the spool had been dipped in a glaze so as to protect the platinum.

The bulb and wires were protected by a closed end copper sheath, the spool being electrically insulated from the metal walls by a wrapping of mica.

In this temperature measuring outfit a number of thermometers were connected to the one indicator and could be plugged in as desired.


Mica washer.
Thin fireclay tubing around lead.
Heavy gold leads.
Wrapping of thin sheet mica.
Winding of fine platinum wire.
Porcelain bobbin.
Closed end copper tube.
70
60
50
40
30
20
10
0
F

Industrial form of Resistance Thermometer.

Mercury thermometer with wooden sheath and lagged. (Mr A.R.T. Wood's design).

FIG. 1.

CALIBRATION OF LOW TEMPERATURE THERMOMETERS.

The calibration of the thermometers below 0° C. was carried out in the apparatus shown diagrammatically in Figs. 2 and 3.

*Description of Apparatus.*—For plain mercury and spirit thermometers the apparatus shown in Fig. 2 was used. It consists of a Dewar vacuum vessel (not silvered), fitted with a "drawing off" pipe for emptying.

A tube projects into the vessel containing a shaft with propeller blades. When the motor is in action, the liquid is sucked up the central tube and discharged out through the orifices, thus ensuring a thorough stirring of the contents. The thermometers are carried on clips attached to the tube and are totally immersed; the readings being taken through the transparent walls of the vacuum vessel.

The liquid employed is clean anhydrous ether. The temperature is lowered by adding successive quantities of carbon dioxide snow.[1]

By means of this apparatus any desired temperature down to − 60° C. may be obtained.

This method was devised about ten years ago by Messrs. Kaye and Higgins for the routine test of low temperature thermometers and the original vessel still survives.

The distant reading mercury thermometer and the resistance thermometer were calibrated in the apparatus shown in Fig. 3, as they were too large to be inserted into the vacuum vessel.

This apparatus was also used for finding the "time lag" of the different types. It consists of a box measuring 2 feet by 2 feet by 2 feet within which is a rectangular spiral of iron piping. This spiral is connected to the refrigerating plant and, by the circulation of the expanded ammonia, the temperature of the air within the box can be lowered rapidly to a minimum of about 35 C.

The bulb of the instrument under test projects into the enclosure and has strapped to it a number of thermo-junctions of copper constantan.

The temperature of the enclosure is maintained steady by observations of the temperature of a thermo-junction suspended freely, as shown in Fig. 3.

It may be remarked in passing that the above methods of calibrating are not applicable to thermometers inserted in pipe lines and which usually have an emergent column. With such thermometers it is desirable to carry out the tests under conditions closely similar to those obtained in practice.

An apparatus which we have found satisfactory for such tests is a small cast iron box inserted in a pipe line connected through a pump to the cold brine reservoir.

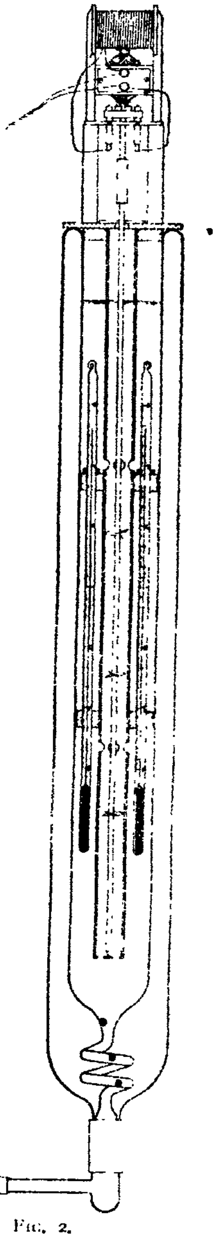


FIG. 2.

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[1] Carbon dioxide snow is prepared as required by allowing the liquid carbon dioxide, sold in cylinders, to expand into a perforated container.

The thermometers are screwed into sockets in the top of the tank and a circulation of cold brine maintained during the test.

### THE "TIME LAG" OF THE DIFFERENT TYPES OF THERMOMETERS.

The apparatus shown in Fig. 3 was used. The procedure was to lower the temperature of the enclosure down to a point corresponding to the lowest scale reading of the thermometer under test and allow it to settle there. The thermometer, initially at room temperature, was rapidly inserted into the enclosure and observations of apparent temperature taken at successive time intervals.

The type of curves obtained will be seen from an inspection of Fig. 4 and, as they are exponential in character, the observations can be shown graphically on a series of straight lines by plotting the logarithm of the temperature excess against the time. See Fig. 5.

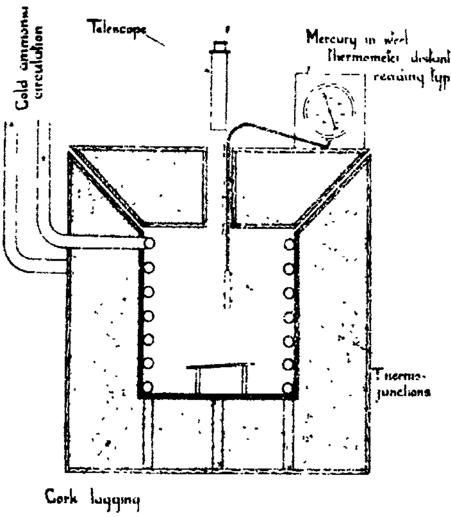

FIG. 3.

The slope of these lines determines the relative "time lags," *i.e.* the smaller the slope the greater the time taken to settle to equilibrium.

For if the thermometer is at a temperature $\theta$ and the enclosure at U, the rate at which the thermometer takes up heat is proportional to $(U - \theta)$. Thus the rate, $\frac{d\theta}{dt} = \frac{1}{L}(U - \theta)$ where $\frac{1}{L}$ is a constant of proportionality and L has the dimensions of a time.

This equation may be written :—

$$\frac{d\theta}{\theta - U} = -\frac{dt}{L} \text{ which gives, if } U = \text{constant,}$$

$$\log(\theta - U) = -\frac{t + a}{L} \quad . \quad . \quad . \quad . \quad (1)$$

To determine $a$, we note that when $t = o$, $\theta = \theta_0$.

Thus $$\log(\theta_0 - U) = -\frac{a}{L}.$$

So that substituting in (1) we get—

$$\log(\theta - U) = -\frac{t}{L} + \log(\theta_0 - U) \quad . \quad . \quad . \quad (2)$$

It is the quantity on the left which is plotted against $t$ in Fig. 5 and we see therefore that the slope of the lines in Fig. 5 is $-\frac{1}{L}$. (In that figure the logs are to base 10, so that the slope has to be multiplied by $0{\cdot}4343 = \log_{10}e$ to obtain $-\frac{1}{L}$.)

Equation (2) gives us—

$$\log\frac{\theta - U}{\theta_0 - U} = -\frac{t}{L},$$

*i.e.* $(\theta - U) = (\theta_0 - U)e^{-\frac{t}{L}}$, which shows that the experimental curves are exponential.

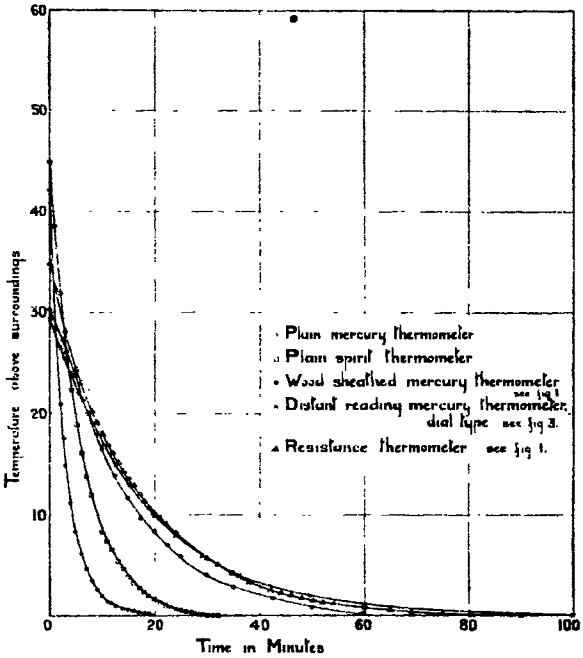

FIG. 4.

Hence when

$$t = L$$

$$(\theta - U) = (\theta_0 - U)e^{-1},$$

*i.e.* the difference is reduced to $\frac{1}{e}$ of its original value.

For this reason L is a convenient constant by which to measure the time lag. A mere statement of its value in seconds or minutes for a particular thermometer is all that is required to determine the behaviour of that instrument under any circumstances as regards time lag.

In particular if the instrument has been taken from one room to another where the temperature is lower by T°, we can see the way in which it will take up the new temperature.

In a time L secs. it will still have 0·368 T° to fall, and this is reduced to 0·000045 T in 10 L secs.

*Experimental Results and their Application.*—From the experiments

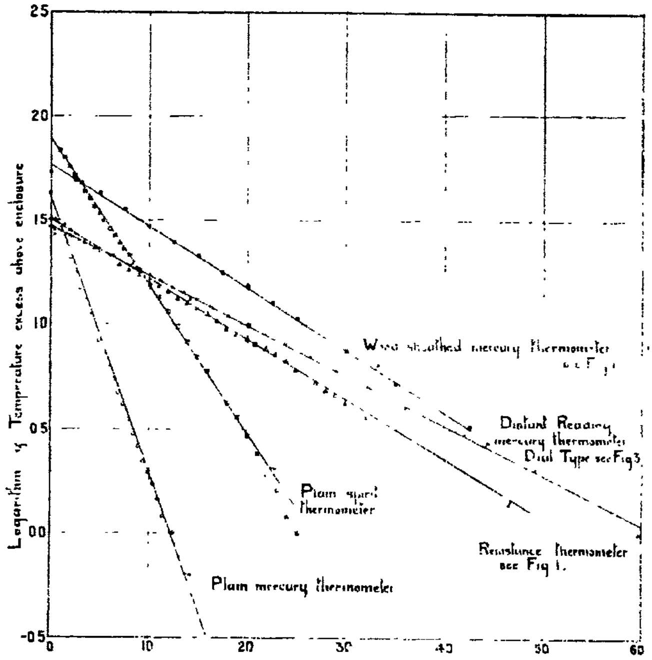

FIG. 5.

described with the various types of thermometers the values determined for the particular thermometers are given below:

| Plain Mercury. (Minutes.) | Spirit Thermometer. (Minutes.) | Wood-sheathed Mercury Thermometer. (Minutes.) | Direct Reading Platinum Thermometer (Minutes.) | Mercury in Steel Thermometer Distant Reading Type. (Minutes.) |
|---|---|---|---|---|
| 3·38 | 6·11 | 14·57 | 17·29 | 18·28 |

The following table, calculated from the above figures, shows the errors introduced in the determination of the temperature of an enclosure such as a ship's hold if the thermometer is first brought to a place where the temperature differs from that of the enclosure by N, and held there *t* secs. before reading. The corrections are true in Fahrenheit units if N is so expressed and in Centigrade if N is measured in °C.

## TABLE.

### Error Introduced in the Determination of a Temperature if the Thermometer is first held for *t* secs. at a Temperature N° Higher or Lower.

| *t* secs. | N | Bare Mercury Thermometer | | | | | [illegible] Thermometer | | | | | Wood-encased Mercury Thermometer. | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 50°. | 55°. | 60°. | 65°. | 80°. | 50°. | 55°. | 60°. | 65°. | 80°. | 50°. | 55°. | 60°. | 65°. | 80°. |
| 0 | | 0·00 | 0·00 | 0·00 | 0·00 | 0·00 | 0·00 | 0·00 | 0·00 | 0·00 | 0·00 | 0·00 | 0·00 | 0·00 | 0·00 | 0·00 |
| 10 | | 1·92 | 2·64 | 2·88 | 3·12 | 3·84 | 1·09 | 1·49 | 1·63 | 1·77 | 2·18 | 0·45 | 0·62 | 0·68 | 0.74 | 0·90 |
| 20 | | 3·76 | 5·16 | 5·64 | 6·10 | 7·52 | 2·15 | 2·66 | 3·23 | 3·50 | 4·30 | 0·91 | 1·25 | 1·36 | 1·47 | 1·82 |
| 40 | | 7·17 | 9·87 | 10·77 | 11·07 | 14·35 | 4·19 | 5·76 | 6·28 | 6·80 | 8·38 | 1·81 | 2·49 | 2·72 | 2·95 | 3·62 |
| 60 | | 10·25 | 14·10 | 15·38 | 16·66 | 20·50 | 9·12 | 7·95 | 9·18 | 10·71 | 12·24 | 2·65 | 3·65 | 3·98 | 4·31 | 5·30 |
| 120 | | 17·87 | 20·83 | 21·81 | 22·79 | 35·74 | 11·30 | 13·51 | 16·95 | 18·36 | 22·59 | 5·11 | 7·02 | 7·66 | 8·30 | 10·22 |
| 180 | | 23·54 | 32·37 | 35·31 | 38·25 | 47·08 | 15·70 | 21·39 | 23·55 | 25·51 | 31·30 | 7·13 | 10·22 | 11·15 | 12·08 | 14·86 |

*Note I.*—If the temperature to be observed is lower than the one in which the thermometer is read, the above corrections should be subtracted from the observed readings.

*Note II.*—The actual values above given are for a particular specimen of each type and would not be true for all thermometers of that type.

It may be worth noting, further, that the constant L has another interpretation. Namely, if the temperature of the enclosure is changing uniformly, the thermometer records the temperature which existed L minutes previously. To show this we have to return to the equation previously given, *viz.*

$$\frac{d\theta}{dt} = \frac{1}{L}(U - \theta).$$

But U is not now a constant. Say it is $U_0 + rt$ where $r$ = the rate at which the enclosure is rising in temperature.

Then $$\frac{d\theta}{dt} = \frac{1}{L}(U_0 + rt - \theta).$$

It may be verified that the solution of this equation is

$$\theta = U_0 + r(t - L) + Ae^{-\frac{t}{L}}.$$

We determine A by putting $\theta = \theta_0$ when $t = 0$ and the equation becomes

$$\theta = U_0 + r(t - L) + (\theta_0 - U_0 + rL)e^{-\frac{t}{L}}.$$

Now if $t$ is large, the last term becomes negligible, and

$$\theta = U_0 + r(t - L) = U - rL \text{ (since } U = U_0 + rt),$$

which means that the thermometer, however long it has been in the enclosure, records a temperature less by $rL$ than the correct temperature, *i.e.* the temperature which existed L minutes previously.

To give some examples of the use of these figures.

CASE 1.—*Temperature of ship's hold rising and observations taken with the distant reading mercury thermometer.* Let us suppose the temperature is required at 12 noon on a certain day and that readings are taken at times 11.50 and 12.10, the values being 39·7° F. and 40·8° F. respectively. Since the lag of this particular thermometer is 18·28 minutes, the hold was at these temperatures at 11 hours 31·72 minutes and 11 hours 51·72 minutes respectively. It is rising at the rate of 1·1° in 20 minutes and therefore in 8·28 it will rise 0·46° F. Thus at noon, the hold temperature is 40·8° + 0·46° = 41·3° F., whereas the mean of the thermometer readings was only 40·25° F.

CASE 2.—*Temperature of hold steady: observations taken by withdrawing the mercury thermometer.*—Assume that the mercury thermometer has had time to settle to temperature of the hold, is withdrawn at 11·50, and read 25 seconds later on deck which is at 90° F.: withdrawn again at 12.10 but an interval of 40 seconds elapses before the reading is taken. Suppose the readings are 38·2° F. and 39·8° F. Then in the first case the value of N in the table is 90 − 38° = 50° F. and $t$ is 25 seconds. From the table the error is 0·22° F. so that the corrected reading is 37·98° F. For the second observation N is again 50° but $t$ = 40 so the error is 1·80° F. and the corrected value 38·00° F. This example illustrates the danger of assuming that the hold is rising in temperature merely by noting two readings without correcting for the lag error.

CASE 3.—*Temperature of hold rising, observations taken by withdrawing the spirit thermometer.* The case considered is that of a ship's hold at about 40° F. and the deck at 95° F.

The thermometer is withdrawn at 11.50 and read after a lapse of one minute and then replaced. The reading obtained is 39·7° F. It is then withdrawn again at 12.10 and read after a lapse of 40 seconds, the reading being 40·8° F. On correcting these observations for the rise after withdrawal by means of the above table, we get for the readings in the hold at 11.50 and 12.10 the values 39·7 − 7·65 = 32·05° F. and 40·8 − 5·76 = 35·04° F. respectively.

Now the reading at 12 noon would appear to be the mean of these, *viz.*, 33·54 F. but owing to the fact that the hold temperature is changing the lag of the thermometer introduces an error in this also. For each of these temperatures existed L mins. previously (L in the case of this particular thermometer being 6·11 mins.) so that at 11 hrs. 53·89 mins. the hold temperature was 33·54° F. It is rising at the rate of (35·04° − 32·05°) in 20 mins., *i.e.* 2·99° F. in 6·11 mins. so that at noon the correct value of the hold temperature was 33·54 + 6·11/20 × 2·99 = 34·45° F.

CASE 4.—*Conditions identical with Case 3 except that Wood's pattern lagged thermometer was employed.*—Reading in hold at 11.50 corrected by table for the deck temperature

$$39·7° - 3·65° = 33·05° \text{ F.}$$

Reading in hold at 12.10 corrected = 40·8° − 2·49° = 38·31° F.

Rate of rise = 38·31 − 33·05° = 5·26° F. in 20 mins.

Now the thermometer lags behind the hold by 14·6 mins., therefore temperature of hold = 38·31° F. at a time 14·6 mins. before 12.10, *i.e.* at 11 hrs. 55·4 mins. A.M.

So the reading of the thermometer at 12.10 is still 4·6 mins. behind the true noon temperature of the hold.

$$\therefore \text{Temperature of hold at 12 noon} = 38·31 + 4·6 \times \frac{5·26}{20} = \underline{39·52° \text{ F.}}$$

As a rule the temperature of the hold does not change at a notable rate so the correction for change of temperature of the hold would be of negligible magnitude. Even in the above case it is only about 1° while that due to the reading being taken on deck is of the order of 6° to 8° F.

The above examples have been constructed to illustrate variations of all conditions, but for comparison of the various thermometers considered, the following table is appended, showing the magnitude of the errors of each thermometer under the same conditions.

*Error in determining the temperature of a space introduced by lag effects.*—

Rate of rise of store = 6° F. per hour.

Rate of fall for values in brackets ( ) = 3° F. per hour.

The thermometer is taken out at the time when the true temperature is required, and read after 40 seconds in a space where the temperature is 80° F.

| Thermometer | Reading. ° F. | Error Due to Withdrawal ° F. | Error Due to Rise of Enclosure. ° F. | Total Error. ° F. | Corrected. Value ° F |
|---|---|---|---|---|---|
| Plain mercury . | 46·3 | + 7·17 | − 0·34<br>(+ 0·17) | + 6·83<br>(+ 7·34) | 39·5<br>(39·0) |
| Spirit thermometer . . | 43·1 | + 4·19 | − 0·61<br>(+ 0·31) | + 3·58<br>(+ 4·50) | 39·5<br>(38·6) |
| Wood's pattern-lagged thermometer . | 39·9 | + 1·81 | − 1·46<br>(+ 0·73) | + 0·35<br>(+ 2·54) | 39·5<br>(37·4) |
| Direct reading electrical thermometer . | 37·8 | — | − 1·73<br>(+ 0·86) | − 1·73<br>(+ 0·86) | 39·5<br>(36·9) |
| Distant reading mercury thermometer . | 37·7 | - | − 1·83<br>(+ 0·91) | 1·83<br>(+ 0·91) | 39·5<br>(36·8) |

# SOME MATERIALS OF LOW THERMAL CONDUCTIVITY.

By Ezer Griffiths, D.Sc., National Physical Laboratory.

*Some Materials of Low Thermal Conductivity.*—From the point of view of the refrigerating engineer, the ideal material for cold storage insulation would be an assemblage of minute gas cells totally enclosed in a light framework impervious to moisture. Hermetical sealing of the cells is essential, for a water logged material is useless for insulation purposes. Besides the fact that the value of the thermal conductivity of water is about ten times that of the conductivity of the materials usually employed for insulating purposes, the presence of moisture is liable to set up decomposition in substances of organic origin. Consequently many excellent thermal insulators, such as cotton waste and wood sawdust, are ruled out on account of their rapid deterioration in the presence of water.

Another important factor which has to be considered in assessing the value of an insulator, especially for marine work, is the weight per cubic foot of the material. A modern refrigerating ship of 6400 tons requires about 400 tons of cork.[1] So a saving of a few per cent. is well worth while.

A material of low weight per cubic foot has the additional advantage

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[1] The following particulars concerning two ships of the Nelson Line were kindly supplied by Mr. A. R. T. Woods, M.I.Mech.E., M.I.N.A.

Ship built in 1911. Registered gross tonnage 7,[illegible] tons. Insulated throughout:—
*Approx. Weights.*

| | |
|---|---|
| Hull, engines and boilers | 449 tons. |
| Refrig. machinery and brine piping, etc. | 610 ,, |
| Insulation, silicate cotton and timber | 1050 ,, |
| Empty ship, total weight | 6150 tons. |

Total capacity of cargo spaces [illegible] cubic feet.
,, ,, ,, ,, [illegible] tons chilled meat.
,, ,, ,, ,, [illegible] ,, frozen meat.

Ship built in 1920. Registered gross tonnage [illegible] tons. Insulated throughout.—
*Approx. Weights.*

| | |
|---|---|
| Hull, engines and boilers | 4624 tons |
| Refrig. machinery and brine piping, etc. | 680 ,, |
| Insulation, granulated cork | 430 ,, |
| ,, timber | 660 ,, |
| Empty ship, total weight | 6400 tons. |

Total capacity of cargo spaces 414,570 cubic feet.
,, ,, ,, ,, 940 tons chilled meat.
,, ,, ,, ,, 4170 ,, frozen meat.

| | |
|---|---|
| Silicate cotton (packed) | 22 lbs. per cubic foot. |
| Cork (granulated) ,, | [illegible] |

that the heat which has to be abstracted in cooling down the stores is less, and this leads to economy of working.

The heat insulators in common use at the present day are slab cork, granulated cork, slag wool, and charcoal. These are so well known as not to need further description[1] and the purpose of the present communication is to bring to the attention of refrigerating engineers a few materials which may be worthy of study under practical cold storage conditions, for they possess at least one essential characteristic of a cold stores insulator, namely, low thermal conductivity.

*Expanded Rubber.*—Methods have been devised for the conversion of rubber into a highly cellular form, the resulting product having an exceedingly low density.

When viewed under a low power microscope, the material shows a structure apparently made up of minute cells bounded by rubber membranes. The cellular structure of the material immediately suggests the possibility of its use as a heat insulator.

The small samples we obtained differed considerably as regards density and presumably this variable can be controlled by the method of manufacture as well as its physical state, whether soft or hard. Samples of the soft variety varied in density from 0·059 to 0·12 C.G.S. units (3·7 to 7·5 lbs. per cubic foot), while a hard variety resembling ebonite had a density of 0·17 (10·6 lbs. per cubic foot).[2]

It would be a matter of considerable theoretical interest to ascertain the relation between the density of the sample and its thermal conductivity, but sufficient material has not been available for such tests. The conductivity of some of the material in sheet form has been determined and varied from about 0·00009 to 0·00012 C.G.S. units, the actual value being dependent, apparently, upon the precise method of manufacture, etc.

Now the weight per cubic foot of the samples tested was only about 5 to 7 lbs., whereas slab cork weighs 11 to 13 lbs. so that when comparisons are made on the basis of the weight of equivalent amounts of insulation the rubber shows a marked saving.

Tests of the insulating value of expanded rubber clippings when packed into an interspace have also been carried out. The clippings had been prepared from a sheet and measured roughly ½ inch × ¼ inch × ¼ inch blocks with considerable variations from the mean. A density determination on some of the fragments gave the value 0·09 ± ·02, *i.e.* 5·62 ± 1·25 lbs. per cubic foot.

In the test the material was evenly packed on either side of a hot plate measuring 8 inches by 8 inches surrounded by a 2 inch guard ring. The thickness of each layer was 1⅛ inches.

In the first test the packing was light, the material being pressed down slightly. The weight of material per cubic foot under these conditions was 2·6 lbs.

The data obtained are given in Table I. below.

The material was then taken out of the apparatus and repacked uniformly, but pressing in as much as possible. The weight of material per cubic foot under these conditions was 4 lbs. The closer packing has increased the insulating efficiency by 12 per cent. (See Table I.)

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[1] Data as to the thermal conductivity of these materials will be found in Special Report No. 5 of the Food Investigation Board entitled *Report on Heat Insulators*, published by H.M. Stationery Office.

[2] The density of ordinary red rubber vulcanised is variable. Two samples gave 1·31 and 1·77, *i.e.* 82 and 110 lbs. per cubic foot respectively.

So it would appear that in a granulated form the same insulating efficiency can be obtained with approximately half the weight of this material, as compared with granulated cork and about one-quarter the weight when compared with slab cork.

A somewhat parallel case to this, as regards the difference in weight per cubic foot, granulated and in sheets, is given by cork. In the baked slab form cork weighs about twice as much as the granulated and gives roughly the same insulating efficiency.

Since it is possible to control, in the course of manufacture, the density of the expanded rubber it would be of interest to ascertain the limit to which the reduction in density can be carried.

TABLE I.

CLIPPINGS OF EXPANDED RUBBER.

*Density of Packing, 2·6 lbs. per cubic foot.*

| Date. | | Time. | Cold Face Temperatures. | | Hot Face Temperatures. | | Mean Temp. of the Material. | | Conductivities. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Cent. | Fahr. | Cent. | Fahr. | Cent. | Fahr. | C.G.S. Units. | B.T.U.'s per sq. ft. per Hour for 1" Thickness and for 1° F. diff. in Temp. |
| Aug. | 7th | 11 A.M. | 20 | 68 | 50 | 122 | 35 | 95 | 0·000122 | 0·342 |
| ,, | 8th | 9 A.M. | 20 | 68 | 50 | 122 | 35 | 95 | 0·000117 | 0·340 |
| ,, | 9th | 12 A.M. | 20 | 68 | 50 | 122 | 35 | 95 | 0·000118 | 0·342 |
| | | | | | | | Probable value | | 0·000118 | 0·342 |

*Density of Packing, 4·0 lbs. per cubic foot.*

| Date. | | Time. | Cent. | Fahr. | Cent. | Fahr. | Cent. | Fahr. | C.G.S. Units. | B.T.U.'s |
|---|---|---|---|---|---|---|---|---|---|---|
| Aug. | 13th | 11 A.M. | 20 | 68 | 50 | 122 | 35 | 95 | 0·000105 | 0·305 |
| ,, | 14th | 9 A.M. | 20 | 68 | 50 | 122 | 35 | 95 | 0·000107 | 0·311 |
| ,, | 15th | 10 A.M. | 20 | 68 | 50 | 122 | 35 | 95 | 0·000105 | 0·305 |
| | | | | | | | Probable value | | 0·000106 | 0·308 |

The material differs markedly from ordinary vulcanised red rubber in its properties, a notable characteristic being its softness. The questions of the durability of the material under rough usage and its chemical stability are ones which merit careful investigation.

Rubber is permeable to water vapour and to many gases, so the gas cells cannot be regarded as hermetically sealed. A sample of the material tested under water for a period of 300 hours showed a progressive increase of weight with time. It cannot yet be stated whether this water absorption is due to water vapour permeating the rubber and forming an adsorbed film on the surface of the cells, or whether it is due to capillary absorption similar to the effect obtained with charcoal. The fact that the action is slow would appear to indicate that it is due to water vapour permeating through the rubber, but it must be remembered that in the case of capillary attraction the action would be slow if the capillaries were close-ended and the water had to dissolve the gas as it flowed along the capillary.

The constitution of the material does not appear to be simply one of gas enclosed in cavities with solid rubber walls, and it is probable that an appreciable amount of gas is absorbed in the rubber. The determination of the state in which the gas is present in the material is a perplexing chemical problem.

In the present stage of our knowledge concerning this new material, it is difficult to express an opinion as to its value as a practical heat insulator for lining the walls of a store. A long period test on a reasonably large scale is really essential, and the quantity of material necessary for such a test has not yet become available.

*Balsa Wood.*—Balsa is the wood of a large tropical tree growing in Ecuador. It is probably the lightest wood known. The samples we have tested have varied in weight from 5·7 to 8·6 lbs. per cubic foot.[1]

As a structural material it is decidedly weak and liable to damage by blows, etc., but it has the advantage over materials such as cork that it can be worked with ordinary wood-working tools which, however, must be very sharp and run at high speed.

In the natural state the wood is subject to decay, but it is claimed that with preservatives it is possible to make the wood sufficiently waterproof to enable it to be used for cold storage insulation.

When the material is to be employed in dry situations it can be surfaced with a veneer of hard wood.

The results of tests on several varieties of the material are given in Table II. below :—

TABLE II.

BALSA WOOD.

*Specimen of 2" Board weighing 5·75 lbs. per cubic foot.*

| Date. | Time. | Cold Face Temperatures. | | Hot Face Temperatures. | | Mean Temp of the Insulating Material | | Conductivities. | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | C.G.S. Units. | B.T.U.'s per Hour per sq. ft. for 1" Thickness and for 1° F. diff. in Temp. |
| | | ° Cent. | ° Fahr. | ° Cent. | ° Fahr. | ° Cent. | ° Fahr. | | |
| March 4th | 8 P.M. | 11 | 52 | 75 | 167 | 43 | 109 | 0·000112 | 0·326 |
| „ 5th | 2 P.M. | 10 | 51 | 76 | 168 | 43 | 109 | 0·000114 | 0·332 |
| | | | | | | Probable value | | 0·000113 | 0·329 |
| *Specimen of 2" Treated Board weighing 8·6 lbs. per cubic foot.* | | | | | | | | | |
| July 28th | 5 | 26 | 79 | 60 | 140 | 43 | 109 | 0·000121 | 0·351 |
| „ 29th | 11 A.M. | 26 | 79 | 60 | 140 | 43 | 109 | 0·000133 | 0·386 |
| „ 31st | 10 A.M. | 26 | 79 | 60 | 140 | 43 | 109 | 0·000129 | 0·374 |
| | | | | | | Probable value | | 0·000130 | 0·377 |

*Fibres of Kingia Australis.*—The possibility of using this material was suggested by Mr. R. A. Fowler, Forest Produce Laboratory, Perth, Australia, who supplied the following information concerning it.

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[1] This may be compared with mahogany, which weighs about 45 lbs. per cubic foot.

It is a fibrous waste from a tree known as "Kingia Australis." This plant is peculiar to Western Australia where it grows on the poorer soils of the coastal belt. The tree consists of a long cylindrical stem up to about 20 feet high and a foot in diameter, surmounted by a tuft of long grass-like leaves. The stems are usually black in outward appearance, owing to charring by forest fires, and are composed of an outer sheath of persistent leaf bases packed very closely together, an inner sheath an inch to 2 inches in thickness of longitudinal fibres cemented together in a close matrix, and an inner core of closely packed short fibres. The inner sheath of long fibres is the only portion of the plant at present used.

A waste product is obtained in cleaning the fibres from the cementing matrix in the form of dust and fibrous material.

The results of a series of tests on this material are given in Table III below :—

TABLE III.

FIBRES OF WOOD, KINGIA AUSTRALIS.

*Density of Packing, 8·4 lbs. per cubic foot.*

| Date | Time | Cold Face Temperatures | | Hot Face Temperature | | Mean Temp. of the Material | | Conductivity | |
|---|---|---|---|---|---|---|---|---|---|
| | | Cent. | Fahr. | Cent. | °Fahr. | Cent. | Fahr. | C.G.S. Unit | B.T.U. per sq. ft. per Hour for 1" Thickness and for 1° F. diff. in Temp. |
| Aug. 27th | 9 A.M. | 16 | 61 | 32 | 90 | 24 | 75 | 0·000118 | 0·342 |
| " 28th | 10 A.M. | 16 | 61 | 32 | 90 | 24 | 75 | 0·000117 | 0·339 |
| " 29th | 11 A.M. | 16 | 61 | 32 | 90 | 24 | 75 | 0·000115 | 0·334 |
| " 30th | 11 A.M. | 16 | 61 | 32 | 90 | 24 | 75 | 0·000117 | 0·339 |
| " 31st | 11 A.M. | 16 | 61 | 32 | 90 | 24 | 75 | 0·000117 | 0·339 |
| | | | | | | Probable value | . | 0·000117 | 0·339 |

*Eel Grass Mats.*—This material is made up of cured eel-grass sewn in between sheets of strong paper. The grass grows in salt water and contains silicon to a large extent. It does not harbour insects or vermin, which is a most valuable characteristic.

The value of eel grass as a thermal insulator appears to have been realised at an early date in the United States, for it is stated that a dwelling house built in 1635 in Dorchester, Mass., was lined with the grass stuffed between the studding, and the material appears to have been in a good state of preservation after a lapse of more than two and a half centuries.

A sample of commercial matting was obtained and tested in two states of packing. The results are given in Table IV.

Whether the material will meet the stringent requirements of the refrigerating engineer is a matter for experiment under service conditions.

### TABLE IV.

EEL GRASS MATS.

*Density of Packing, 9·4 lbs. per cubic foot.*

| Date. | | Time. | Cold Face Temperatures. | | Hot Face Temperatures. | | Mean Temp. of the Material. | | Conductivities. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Cent. | Fahr. | Cent. | Fahr. | Cent. | Fahr. | C.G.S. Units. | B.T.U.'s per sq. ft. per Hour for 1" Thickness and for 1° F. diff. in Temp. |
| May | 8th | 10 A.M. | 15 | 59 | 45 | 113 | 30 | 86 | 0·000109 | 0·318 |
| ,, | 9th | 9 A.M. | 15 | 59 | 45 | 113 | 30 | 86 | 0·000105 | 0·314 |
| | | | | | | | Probable value | | 0·000108 | 0·316 |

*Density of Packing, 13·4 lbs. per cubic foot.*

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| May | 10th | 11 A.M. | 19 | 66 | 41 | 106 | 30 | 86 | 0·000117 | 0·341 |
| ,, | 17th | 11 A.M. | 19 | 66 | 41 | 106 | 30 | 86 | 0·000117 | 0·341 |
| | | | | | | | Probable value | | 0·000117 | 0·341 |

*Compressed Peat.*—Peat, variously treated, is being extensively used on the Continent for heat insulation. The chief merit of the material is its cheapness. For cold storage work the peat is impregnated with a bituminous substance to protect it from the effect of damp. Data concerning tests on "treated" and "untreated" material are given in Table V. below.

The heavy weight per cubic foot of the material—20 to 30 lbs.—is a disadvantage.

### TABLE V.

COMPRESSED PEAT.

*Weight of Specimen, [illegible] lbs. per cubic foot.*

| | | Time. | Cold Face Temperatures. | | Hot Face Temperatures. | | Mean Temp. of the Material. | | Conductivities. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Cent. | Fahr. | Cent. | Fahr. | Cent. | Fahr. | C.G.S. Units. | B.T.U.'s per sq. ft. per Hour for 1" Thickness and for 1° F. diff. in Temp. |
| Aug. | 7th | 10 A.M. | 23 | 73 | 51 | 124 | 37 | 99 | 0·000175 | 0·509 |
| ,, | 8th | 10 A.M. | 23 | 73 | 51 | 124 | 37 | 99 | 0·000176 | 0·512 |
| | | | | | | | Probable value | | 0·000176 | 0·512 |

PEAT TREATED WITH BITUMINOUS MATERIAL.

*Weight of Specimen, 29·5 lbs. per cubic foot.*

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Aug. | 19th | 11 A.M. | 24 | 75 | 52 | 126 | 38 | 100 | 0·000175 | 0·507 |
| ,, | 20th | 11 A.M. | 24 | 75 | 52 | 126 | 38 | 100 | 0·000173 | 0·501 |
| ,, | 21st | 10 A.M. | 24 | 75 | 52 | 126 | 38 | 100 | 0·000173 | 0·502 |
| | | | | | | | Probable value | | 0·000173 | 0·502 |

A sample obtained from another source gave the value 0·000167 C.G.S. units for the thermal conductivity at 38° C.

In conclusion it may be pointed out that the thermal conductivity of insulating materials in general is not an invariable physical constant. So, it follows that it is advisable to test samples of various consignments just as it is desirable to determine the calorific value of a fuel.

The experiments recorded in this paper and the other on Thermometric Lag constitute a part of the programme of work for the Engineering Committee of the Food Investigation Board.

We desire to record our thanks to the Engineering Committee and to our director for their interest and encouragement.

# THE METALLURGICAL ASPECT OF THE PRODUCTION OF COLD.

By Cosmo Johns.

Most of the useful metals in present-day practice are extracted from their ores, and refined for the use of man, by processes which involve the use of atmospheric air for the combustion of carbonaceous matter, silicon, phosphorus or sulphur to provide the heat required. These processes have become standardised to a large extent and are based on the assumption of the invariableness of the oxygen content of the atmosphere. Until Gayley, not so long ago, demonstrated that the seasonal variations in the aqueous vapour content of the atmosphere could be controlled in the air blown into the blast furnace by refrigeration, it had been assumed that the fluctuating aqueous vapour content of the atmosphere was beyond human control in metallurgical operations on a commercial scale. To-day the assumption of invariability in the oxygen ratio of the air used is firmly rooted in the minds of those who are operating metallurgical plants.

Obviously the oxygen enrichment of the air used would alter the conditions under which those metallurgical processes which depend on oxidation of some fuel for the heat required are carried out; and though it is difficult to predict what would actually be the effect of such altered conditions yet enough is known to enable us to say that revolutionary changes in metallurgical practice would result. The processes now employed, and the types of plant used, are the result of gradual evolution of industrial practice. Our knowledge of the reactions that occur are imperfect and almost entirely restricted to our knowledge of what occurs when ordinary air is used. But though it may be difficult to predict the actual changes in practice that would result, it is comparatively easy to review the possibilities. It is important to note, however, that what is contemplated is not the use of pure oxygen but the availability of a mixture with 30 to 40 per cent. oxygen or even less.

The modern blast furnace plant would obviously undergo a startling change in its design and arrangement when it had no longer to handle the present huge volumes of dust laden heated combustible gases, to effect difficult heat exchanges with the incoming air, to secure fuel economy. The hot blast stoves would probably disappear or be much reduced in size. The furnace itself would be reduced in height and the whole plant, when the changes had been completed, would bear but little resemblance to the equipment found necessary to-day for the production of pig iron. The bessemer converter, whether acid or basic, has been evolved on the assumption of an invariable oxygen content of the air blown in. Given the possibility of varying and controlling the oxygen ratio in the air employed we should find the character of the process completely changed. In the acid process it is known that the order in which carbon and silicon are removed depends on the temperature. In the basic process it is almost certain that by controlling the temperature it would be possible to oxidise the phosphorus before all the carbon had been removed and thus the injurious after blow would be avoided. This temperature control could be effected if the oxygen content of the air blown in could be varied.

The regenerative open hearth steel melting furnace is costly, complicated and inefficient from the thermal standpoint. If oxygen-enriched air could be employed for the production of the fuel gas and for its subsequent combustion in the hearth of the furnace it would be possible to effect a startling and beneficial alteration in the plant. The uni-flow furnace would become a possibility and there would be a very desirable simplification in the design of the plant. A neutral or oxidising flame would be at the command of the operator while the melting and refining operations would be accelerated. The waste gas of the furnace would be much richer in $CO_2$ and with added oxygen rich air would be ideal for blowing into the gas producer thus enabling a fuel gas rich in CO to be supplied to the furnace.

The possibilities of beneficial changes in the practice of copper smelting and refining would be as great as in iron and steel works practice. Pyritic smelting would lose many if not nearly all its difficulties if it were commercially possible to vary the oxygen content of the air used, while the bessemerising of copper matte would be accelerated. Most important of all would be the possibility that the waste gases now difficult to handle owing to the vast volumes of inert gas present, could be used for the recovery of their sulphur content. But it is unnecessary to pursue further this review of metallurgical possibilities once a commercial method of giving an oxygen enriched air is available. Whether the fuel burnt be carbon, silicon, phosphorus or sulphur the result must be to give greater freedom to those operating the various processes and to open the way for new advances in metallurgical practice.

It is important to note that it is not pure oxygen that is required. It would be amply sufficient if the oxygen content could be varied between the range of 20 and 40 per cent. The problem is therefore quite different to that of preparing pure oxygen. Dr. F. G. Cottrell[1] has pointed out in his admirable review of the subject the fact that air is a mixture of oxygen and nitrogen and that the theoretical amount of energy required for the separation of the two gases is very small, in fact only about 1 per cent. of that required for the production of an equal weight of electrolytic oxygen. Now any cycle that requires energy of the order of 30 H.P. per 1000 cubic feet of oxygen at normal pressure and temperature can be ruled out at once. What is required is not pure oxygen in steel bottles but enriched air in hundreds of tons. It can be assumed that in this country the production of a ton of pig iron requires 140,000 cubic feet of air at normal temperature and pressure. This will serve as a measure of the quantities involved.

Owing to the slight difference in density of oxygen and nitrogen it would appear that centrifugal methods for their separation are not very hopeful. Can any refrigerating system be devised which will give oxygen-enriched air at a commercial price? Any such refrigerating system should be able to use, as the source of the energy it requires, the sensible or potential heat of the products of the metallurgical process where it is employed if carbon be the fuel used in that process. If a suitable cycle can be discovered for effecting the partial separation of two mixed gases, for complete separation is not required, then a vast field is available for the use of oxygen enriched air in metallurgical operations. If this cycle cannot be made to operate on lines sufficiently economical then it would appear that the production of cold will not be so attractive as it appeared to be and that the discarded barium oxide process might be re-investigated. Its old fault that it did not give pure oxygen may prove to be one of its virtues. The working temperature at which, with varying pressure, it absorbs or evolves oxygen is fortunately within the range of the now available impermeable alloys which resist oxidation. The temperature required can be supplied by the sensible or potential heat of the waste gases in many metallurgical processes. If refrigeration as a method of giving oxygen enriched air fails us then barium oxide or some substance with similar properties require careful investigation, for mankind in its metallurgical work will not always be content to be controlled by the atmosphere nature provides.

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[1] *Chemical and Metallurgical Engineering*, July 14, 1920, p. 53 *et seq.*

# A NOTE ON THE IMPORTANCE OF THE STUDY OF THE CRYSTAL STRUCTURE AND PROPERTIES OF METALS AT LOW TEMPERATURES.

BY COSMO JOHNS.

It is well known that, in a general way, the properties of the elements are periodic functions of their atomic weight or, as would be stated more correctly now, of their atomic number. Among others Roberts-Austen,[1] Richards,[2] Edwards,[3] Haughton and Ford,[4] have discussed this periodicity with reference to the metals, but all these attempts have disclosed imperfections which can be attributed either to inaccuracies in the data available or to some error in the method adopted for handling them. From time to time it has been pointed out[5] that no true comparison can be made unless the data used have been measured at strictly comparable temperatures. These comparable temperatures can only be known when the crystal structure and significant properties of the metals have been determined over the widest possible range of temperature. Such comparable temperatures will, in all probability, be themselves a periodic function of the atomic number, and should therefore stand in some definite relation to the absolute melting point. It is obvious that to take data relating to properties which are known to vary with temperature, and to use those which have been measured at some temperature level selected for convenience only is to invite confusion, which can only serve to obscure, if not to hide, the relationship which is being investigated.

To mention but a few metals we find, if we examine them at room temperature, that mercury is liquid, lead so plastic that it is self-annealing after severe straining: aluminium displays a marked tendency in the same direction. Copper exhibits marked ductility after quenching from a moderately high temperature. Iron when modified by the presence of carbon loses ductility and acquires greater tenacity when quenched from above a certain critical temperature; when the iron is alloyed with 25 per cent. nickel or 12 per cent. manganese it ceases to behave like carbon steel on quenching, but becomes analogous to copper. This is known now to be due to the lowering of the inversion point by the addition of the alloy metal. Recently it has been demonstrated that iron above the critical range of temperature has a centre face cubic lattice, while below that range it crystallises in the centre body cubic lattice.[6] Copper, manganese steel, and 25 per cent. nickel steel all have the centre face cubic lattice as the feature of their crystal structure at room temperatures. Seeing that properties such as tenacity and ductility depend on crystal structure, and that crystal structure, certainly in some metals and probably in all, will vary above and below some critical temperature which will be different for each metal, the futility of confining the comparison to data collected at one temperature becomes apparent.

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[1] *Proc. Royal Society*, 1891, Vol. xlix., pp. 317-356.
[2] *Faraday Lecture*, 1911, Chemical Society.
[3] *Jour. Inst. Metals*, 1918, No. 2, pp. 56-88.
[4] *Trans. Faraday Society*, 1922, Vol. xviii., Part I., pp. 112-118.
[5] Professor Porter, *Trans. Faraday Society*, 1922, Vol. xviii., Part I., p. 118.

There is, however, another point that requires consideration, and that is the influence of temperature on the tenacity and ductility of metals within the range of temperature over which the same crystal structure prevails. Within this particular range of temperature we must primarily be dealing with the strength of the cementing material that holds the crystals of the solid metal together, and therefore determines its tenacity; and secondly with the ability of the crystal to undergo plastic deformation. This influence of temperature is very profound at the lower ranges of temperature. Metals ductile at room temperatures lose their ductility and become endowed with great tenacity at low temperatures. Some preserve their ductility to very low temperatures. Most of these changes are reversible, but it is possible that some are irreversible. Our knowledge of the influence of structure, using that word in its widest sense, on the strength of metals is very fragmentary. Our methods of measuring that strength, once we have passed outside the range of elasticity, have been, and very justly, the subject of severe criticism.

The information which would probably have the most immediate value would be that relating to crystal structure and strength of the pure metals at the widest possible range of temperature, and the most important would probably be that determined at low temperatures. The most promising method of determining the strength would be the stress-strain diagram carried on to rupture at some definite rate of straining, the time interval being kept as short as possible, with the optical recorder of Dalby.[1] The complete stress strain diagram obtained with this apparatus would give us the required data to enable us to evaluate the diverse properties we now include under the word strength. When our knowledge of the low temperature relationships has been extended and the many gaps in our knowledge of the change of properties and structure have been filled, we shall be able to undertake, with some chance of success, a study of such relationships as a periodic function of the atomic numbers of the metals.

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[1] *Phil. Trans. Roy. Soc.*, A. 5[illegible], 1920, pp. 117-138.

# *DISCUSSION ON "INDUSTRIAL METHODS OF LIQUEFACTION AND PRACTICAL APPLICATIONS OF LOW TEMPERATURES."*

**Mr. C. R. Darling** (*communicated*): Amongst practical devices for the measurement of low temperatures, the convenience of a thermal junction coupled to a suitable indicator is apt to be overlooked. Some years ago, when engaged upon the determination of the congealing points of certain oils and other liquids, I had constructed the instrument now shown, which consists of a flexible couple of Hoskins alloys, and a portable indicator of the pivoted, moving-coil type. Correction for changes in the temperature of the atmospheric junction may be made by adjusting the pointer so that its position on the scale coincides with the reading of a mercury thermometer inserted in the lid of the indicator. The scale was calibrated at the National Physical Laboratory, the lowest reading being − 200° C., and the apparatus proved quite satisfactory in use. Its advantages over a pentane thermometer were that it responded more quickly to changes in temperature, and could be used in metal vessels and enclosures under conditions in which the readings of a pentane thermometer would not have been visible. A recent check of the calibration at the temperature of solid carbon dioxide showed that the instrument had maintained its accuracy. From this experience, I suggest that the thermo-electric method of measuring low temperatures may with advantage be applied in many cases where other methods are now in use.

As a means of determining the temperatures of the different parts of a large cold store, the resistance thermometer is the best at present available. When a number of these are brought to a switchboard, and arranged so as to be capable of connection to a common indicator, much care is needed in the choice of proper materials if good results are to be secured. Recently, when going through a large cold store in London operated by ammonia refrigerators, I observed that the switchboard was located in a small office in the engine room, in an atmosphere smelling perceptibly of ammonia. The fittings on the switchboard, being constructed of brass lightly nickel plated, showed very marked corrosion, and the instrument was out of action. As an installation of this kind is expensive, every care should be taken to avoid mistakes of this kind, which tend to bring discredit on a very useful method of measuring these temperatures, and serve to prevent its more extensive use.

**Dr. J. A. Harker**: Mr. Murray has given us a great deal of information in a very quiet way. He is not a person who is easily persuaded to talk about things, but I think he knows more than any person in the world about the development of the oxygen industry. I was hoping that we should have had another equally interesting industrial authority on oxygen with us, Mr. Price, President of the Union Carbide Co. of America, who is at present in London, but unfortunately he was not able to be present.

The author has told us one or two very important things. We all know how, in the ordinary liquefaction of air, Claude applied Lord Rayleigh's suggestion and used an expansion engine. Mr. Murray has told us something very important about this, and I am able to endorse entirely from my own experience and knowledge what he says. Some few months ago when I was discussing the relative advantages of Claude and Linde plants, Mr. Murray said that the use of the expansion engine was a "talking-point" in favour of the Claude process. I think that statement sums up the situation because since that time I have visited four or five different plants where expansion engines are in use and in almost every instance I noticed that the energy recovered is turned into a resistance coil and is doing no good at all, or at best is only warming the room. It is *never* used as it is figured in the text-books, and turned into the line to diminish the power requirements in the way that theoretical people talk about.

Mr. Murray finished up with a statement about the industrial uses of oxygen, and foreshadowed some uses which have not yet materialised. It is dangerous to prophecy, but I will nevertheless venture to say one thing. The last twenty years of this century may be said to have been the period of the fixation of nitrogen: the next twenty years will in my view be a period in which the greatest industrial advance will be in the application of oxygen to industrial problems. I have good reason for this view, and I think Mr. Murray is right when he says that there are many things foreshadowed, of which we do not yet realise the possibilities.

**Dr. W. M. Travers** said he would like to say a word about the assistance Mr. Murray had given him in his early work on the liquefaction of gases. His firm was then Brin's Oxygen Company, and it was pleasing to hear of the enormous developments which had taken place since those days. We may anticipate even more extensive developments of the oxygen industry, for cheapening of the cost of oxygen must lead to the direct method for completely gasifying coal, which is the goal of all gas technologists.

**Mr. H. Brier:** I should like to say a few words on Mr. Johns' remarks with regard to the use of oxygen for blast furnaces, etc., for I think you would be interested to know the results of an experiment which was made about 1800 with a small Bessemer converter in Glasgow.

Oxygen was then introduced in different percentages into the air blast. At no time was any great quantity of oxygen used, but the results were most disastrous. After a very short time the tuyères and bottom of the converter were consumed and blew out, and those standing by very naturally stood away from the converter expecting the charge to follow, but only a moderate flow of liquid came out into the bottom of the pit, and this was found to be the liquid formed by the melting of the tuyères and lining, all combustible metal having disappeared leaving only a black skull in the top of the converter.

Any experiment of this kind will require to be very carefully made, so that the enriching is not too drastic in its action upon combustible material.

**Dr. E. B. Maxted:** With respect to the running of water-gas furnaces with oxygenated air, I fully endorse the remarks of the last speaker as to what happens. The oxygen is usually mixed with steam or with a diluting agent, but in spite of this, the tendency is for the fire bars to burn away rapidly. It is extremely difficult to moderate the action of the oxygen even by diluting it with steam.

With regard to the general question of the liquefaction and separation of the permanent gases there are, perhaps, one or two points of interest that may be touched on. The first point relates to the complete separation of air into nitrogen and oxygen. Theoretically, the curve connecting the vapour pressure of a mixture of nitrogen and oxygen with the composition of the mixture is such that a separation into pure nitrogen on the one hand and pure oxygen on the other should be possible. As a matter of fact, in most plants, either pure nitrogen or pure oxygen is produced but not the two gases simultaneously, and there would appear to be an opening for a plant in which each of the gases is produced in a state of sufficient purity to be used technically. In most cases, both the nitrogen and the oxygen have to be substantially pure before they are usable. In the majority of plants, according to present practice, either the one or the other gas is run to waste, and it is evident that some modification of the system is required.

My point relates to the drying of the gases. Mr. Murray in his paper referred to the two methods of drying the air or other gas which is being separated, either by chemical absorption, *i.e.*, by means of chemical drying agents, or by refrigeration. If a process of refrigeration is employed, it is extremely interesting to notice that the form in which the moisture comes down depends on the temperature gradient, on the temperature itself, and on other conditions. The moisture may come down either as a solid coherent cake of ice, or as coherent strands which gradually lengthen; or again, as a mass of mobile ice crystals which are easily blown by the gas current into the filter. Of course, this last form is the one which is particularly desirable if the blocking of the drying tube is to be prevented.

The final point I wish to touch on is the necessity, or the desirability at any rate from the general standpoint, for the publication of systematic work on the mechanism of heat exchange. In most cases when we put in a heat exchanger we guess the area from previous experience. There exist at the present time very few published data relating to the actual rate of transfer of heat between two gases at different temperatures separated by metallic surfaces. Of course, it is not possible to calculate this rate of exchange from considerations based on conductivity and viscosity, because of the complicated nature of the motion of the gas particles and, further, because of the formation, particularly at low temperatures, on the exchange surface of a peculiarly sluggish film of gas which hinders the exchange and which is very difficult to attack by turbulence of the remainder of the gas. In any case, I certainly think that a very important field exists for physical research in the general mechanism of heat exchange, and I should like to see more data published on this subject.

It is particularly appropriate that at a discussion of this sort we should have papers from the great cryogenic laboratory at Leyden, whose work we all know so well, and also from M. Claude, who has probably done more than any other man to further the technical production of cold and the technical separation of the so-called permanent gases.

**Professor C. F. Jenkin:** Mr. Griffiths stated that the efficiency of the refrigerating plants was extraordinarily low; I think he said about $1\frac{1}{2}$ per cent. I should like to ask Mr. Murray if he has ever drawn up—I have no doubt that he has—a heat balance for the larger plants. Certainly an efficiency of that sort ought to be able to be enormously improved. The first step, obviously, is to know how bad it really is. The last speaker has mentioned the transfer of heat from metal surfaces to gases. I do not know whether he is aware of a great deal of valuable research work recently done at the National Physical Laboratory in connection with the transfer of heat from cold chamber walls to the air. A complete theory of the transfer of heat from surfaces to the air has been worked out. I do not think that the conditions under which these experiments were made are comparable with those for interchangers, but I think possibly they may form a foundation of a theory for interchangers.

**Mr. A. G. Tarrant:** I should like to ask Mr. Griffiths a question. Those of us who have seen the effect of a bullet on a compressed gas cylinder will realise the enormous advantage of having gas in a somewhat less dangerous form. I should imagine the pilot of an aeroplane will want his apparatus as automatic as possible, but as far as I can make out, about 200 calories per minute will be required to warm the gas up to a breathable temperature. Can Mr. Griffiths tell us how that can be automatically supplied?

**Mr. L. D. Goldsmith:** I should like to ask a question of Mr. Griffiths with regard to the use of liquid oxygen for aeronautical purposes. Was the liquid he used actually oxygen, or was it the mixture of 50 per cent. nitrogen and 50 per cent. oxygen which the ordinary liquefier gives? As apparently no rectifier was used, the liquid was presumably this mixture.

**Mr. Edgar A. Griffiths:** Mr. Tarrant refers to the question of supplying the heat necessary to vaporise the liquid oxygen. The vaporisers are provided with a large area for absorbing heat from the atmosphere and although the surface may become frosted over the heat interchange is not appreciably diminished.

As stated by Mr. Goldsmith the usual liquefier only produces low percentage oxygen, but the liquefiers used for aeronautical work were provided with rectifiers. The oxygen drawn off varied from 75 to 96 per cent. purity with different types of plant. Nitrogen would be mere superfluous weight and bulk in this case.

The Chairman's suggestion of subdividing the interspace between the two walls of a vacuum vessel involves a practical difficulty inasmuch as a good vacuum is not readily obtainable since the packing tends to retain a large volume of gas which is only released very slowly.

**Dr. Ezer Griffiths:** An account of the work on heat transfer referred to by Professor Jenkin will be found in Special Report No. 9 of the Engineering Committee of the Food Investigation Board published by the Stationery Office. It is entitled "Report on Heat Transmission by Radiation and Convection."

**The Chairman (Mr. James Swinburne):** Mr. Edgar Griffiths has referred to the question of making a double sheathing to check radiation by making it in two steps. During the war I suggested that it might be a good thing to fill in the interstices with something like very fine slag wool. I do not know why it should not work. The idea was not used, but I wonder if it is possible to gain more that way than you would lose by conduction. Mr. Griffiths also mentioned cooling by external work. In 1910 I read a paper before this Society[1] on liquefying air and gases, and I remember pointing out that the use of an engine expanding was, theoretically, a mistake. I was dealing there with separating gases and not delivering liquids. I do not remember what my argument was or whether I was right or wrong, but it looks as if the external work engine did not work in practice, and it may be that I was right and that it is not really right theoretically. Dr. Griffiths however was using it for liquefying and not for turning out separated gases, and it is not at all the same problem. In the same paper I remember pointing out the advantage of using oxygen for blast furnaces. Nothing happened, and no one ever tried it as far as I know, until recently. We have now heard of trials and a good deal depends upon the cost. As far as I could see in those days, the cost of the oxygen came out at about 1s. a ton. Of course, that was doing it on a large scale for blast furnaces. In commerce one would not expect the cost to be as low as that, but neither would one expect it to come out at something more than a 1s. a lb. or whatever the figure is that has been mentioned to-night. There must be a large margin.

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[1] *Trans. Farad. Soc.*, 1911, VI., 212.

**Mr. Brier:** The difficulty in using oxygen in the blast furnace is not the question of price or the cost of the oxygen. It is that you get a consumption of metal itself by means of the oxygen. We found all the metal disappeared.

**The Chairman:** I was coming to that. The first point naturally is the price. Gayler was the first to advocate the removal of water vapour in blast furnaces. The blast furnace is very near the margin of not working well and the water vapour interferes. The proposal was not to use air with a whole lot of oxygen so that you cannot get the firebricks to stand up in the furnace, but merely to put a little extra oxygen in, which can be got as has been suggested not by separating completely but with very imperfect separation, just enough to make the temperature right. What one wants is to get the temperature right in blast furnaces, to prevent it being lowered below the normal when there is too much moisture. Very likely there would be no furnace left at all if you blow in a whole lot of oxygen.

Dr. Maxted has asked about the difficulty of two pure gases. To turn out two gases is a question of fractionisation and you can always get a machine that will fractionise at one end and turn out a mixture at the other, but I do not see any conceivable way of getting two pure gases unless with an infinite amount of fractionisation. The only way would be to reject the middle portion of the mixture and so have two pure ends. I should think there is no difficulty in making such a machine, but I should not think you would possibly get two complete separations without a tremendously elaborate machine. With regard to interchangers, heat transmission inside a boiler tube is very much the same sort of thing and I think a good deal of work was done by Professor Nicholson of Manchester, but I cannot remember whether it is the sort of work that Dr. Maxted wants in this particular case.

**Mr. Cosmo Johns,** in reply to the discussion on his paper, wrote that Mr. Swinburne appeared to have effectively dealt with the objections raised. Any changes in the oxygen concentration of the air used for metallurgical purposes would have to be made with great caution. If the oxygen in the air used were increased by 5 per cent. it would mean that it had been raised from the original 20 per cent. to 25 per cent. This is an increase of no less than 25 per cent. on the original percentage. In the experiment referred to by Mr. Brier the increase was probably much more. It is often overlooked that it is the increase in the partial pressure of the oxygen that is the really significant factor in the use of oxygen-enriched air. The available evidence strongly supports the view that variations in the concentration, or partial pressure, of the oxygen would alter the order in which the metals and metalloids are oxidised in the bessemer process for basic steel making. Dilution with steam would be unnecessary in furnaces if air enriched with oxygen to the required and pre-determined proportion had been used. This brings us back to the main argument of the paper. We don't require pure oxygen; we want a process that will enrich the air used with just the percentage required and this increased percentage will probably be, for most metallurgical operations, a comparatively small one. One naturally looks to some method of refrigeration to accomplish this, but if there is no method of refrigeration with the required thermal efficiency available, then we must revert to some other process.

**Dr. Richard Linde** (*communicated from Munich; translated*): The Faraday Society has invited me to send a contribution to this discussion, but only the papers by Mr. Murray and by Mr. Claude call for comments on my part. In limiting myself to the following remarks, I am anxious to express my thanks to the Faraday Society for their courtesy.

Mr. Murray's very apposite historical outline of the development of the oxygen and nitrogen industries hardly requires further remarks. Mr. Murray states that, according to his experience, plants on the Linde system do not work with as favourable an energy consumption as plants on the Claude system; he adds, however, that he was, in making this statement, entirely relying on his own observations. I cannot, on this occasion, enter into details, but I would refer to the paper I published in the *Zeitschrift des Vereines Deutscher Ingenieure* of December 24th, 1921, pages 1356 to 1360. The "Gesellschaft fur Linde's Eismaschinen," which supplies installations on the Linde system, guarantees in plants for 100 m.$^3$ per hour a power consumption not exceeding 1[illegible] h.p. per m.$^3$ of oxygen at atmospheric pressure (3·4 B.H.P. per 100 cubic feet). In larger units the power consumption goes down to 1·0 h.p. for the supply of an oxygen of 98 per cent. The Gesellschaft fur Linde's Eismaschinen has erected a plant of three units, each of 600 m.$^3$ of oxygen per hour, which has permanently been working at this power consumption.

The paper just quoted also gave some figures concerning the recent development of the oxygen and nitrogen industries in Germany. Those figures have already been exceeded. At present more than 2,500,000 m.$^3$ (nearly 100,000,000 cubic feet) of oxygen are put upon the German market every month, in steel cylinders. In addition, a large number of engineering works and shipbuilding wharfs make their own oxygen for autogenous metal working; that oxygen production may be estimated at 1,000,000 m.$^3$ per month. Finally the chemical industry requires very considerable amounts of oxygen which the works likewise generate in their own plants; this oxygen will also exceed 1,000,000 m.$^3$ per month. Thus Germany is at present producing at least 50,000,000 m.$^3$ (1,750,000,000 cubic feet) of oxygen per year.

The amount of nitrogen produced by the liquefaction of air and utilised almost exclusively for the manufacture of fertilisers is considerably larger. I estimate the annual German demand for nitrogen at 300,000,000 m.$^3$ (more than 10,000,000,000 cubic feet).

With respect to Mr. Claude's paper I beg to point out that the manufacture of hydrogen from water gas by fractional condensation was practised in Germany on a very large scale already ten years ago, in installations due to the Gesellschaft für Linde's Eismaschinen. The ammonia works of the Badische Anilin-und Soda fabrik at Oppau, for instance, kept 3 units each for generating 1000 m.$^3$ of hydrogen (in addition to 349 m.$^3$ of nitrogen) in operation for several years; work in this installation was discontinued only because the Badische had meanwhile developed the purely chemical hydrogen process, mentioned by Mr. Claude, which proved better for their purpose. There are other hydrogen plants on the Linde system in operation, *e.g.* in fat-hardening works in Holland. It is true that the Linde company does not produce the low temperatures, which the preparation of pure hydrogen necessitates, with the aid of an expansion cylinder: they do this with the help of a special air liquefaction plant which, in the case of the Badische Anilin-und Soda fabrik, also supplied the nitrogen required for the ammonia synthesis. As regards the energy consumption there is no noteworthy difference between the Claude and the Linde hydrogen processes. We have to consider that, on the Claude system, the hydrogen has first to be expanded in the engine and then to be compressed again for the ammonia synthesis, whilst on the Linde system the hydrogen leaves the apparatus at a pressure of about 20 atmospheres, the pressure under which the water gas is decomposed. At any rate, 1000 m.$^3$ of hydrogen and 350 m.$^3$ of nitrogen were being produced in the period mentioned at Oppau by an expenditure of less than 900 h.p. hours. On the Claude system, the compression of the water gas to 20 atmos., and the recompression of the hydrogen to 20 atmos., would require about 650 h.p. hours, and the production of 350 m.$^3$ of nitrogen nearly 100 h.p. hours. A small, but not negligible portion of the nitrogen has further to be compressed to the pressure of the water gas, for the lubrication of the expansion cylinder. That will absorb a certain amount of energy, and the final difference in power consumption will certainly be small.

The high yield of hydrogen which Mr. Claude claims for his process has also been attained in Linde installations. At Oppau the yield represented about 97 per cent. of the hydrogen entering the separator. Again the carbon monoxide which is formed in the water gas process is also being utilised for power generation in the Linde installations.

I do not dispute that Mr. Claude has solved in a very elegant manner the problem, which is not simple in itself, of cooling the hydrogen down to less than − 200° C. by means of an expansion cylinder, without producing too low a temperature in the cylinder itself. But this solution has some disadvantages. Thus there is doubtless a certain danger that a water hammer effect may occur in the expansion cylinder when the cylinder must contain some liquefied nitrogen. Further, the hydrogen is again contaminated with nitrogen, which is permissible only in synthetic ammonia processes. Yet even in that instance it seems doubtful whether progress is achieved by effecting the production of the cold wanted in the apparatus for the water-gas decomposition by expanding the hydrogen, instead of making the plant for the production of the nitrogen, which is indispensable anyhow, work at a somewhat increased intensity so as to obtain some liquid nitrogen, as is done in plants on the Linde system.

**Mr. K. S. Murray:** In the course of this discussion some speakers have been rather severe in their comments on Claude's expansion engine. It is quite true that in small plants the energy recovered through the expansion engine is usually dissipated in a resistance coil or something of the kind, but there is no reason why it should not be used for such a purpose as charging storage batteries, and that is not infrequently done. Practically all our plants are operated in large cities where electric power is cheap enough to make the recovery of energy from the expansion engine unimportant, but where that is not the case, and more especially where some other form of prime motive power for the plant has to be employed, as in country districts, then undoubtedly the energy developed by the expansion engine can be made use of in a variety of ways. I was, unfortunately, not able to be present at the meeting when Mr. Griffiths read his paper, and I have only seen an abstract of it. I am not, therefore, clear as to what the 1½ per cent. efficiency mentioned by Professor Jenkin refers. If it is the ratio of the theoretical power required to the actual power consumed in producing oxygen by the liquid air process, the result obtained by Mr. Griffiths is very poor. It is true that the best liquid air plants for the production of oxygen are far from theoretical perfection, but, based on the figures which I have given in my paper for the plant producing 4000 cubic feet of oxygen per hour, I think the efficiency will be found to be about 6 per cent. Some 6 kw. are recovered by the expansion engine, and if this energy were utilised in the system, the efficiency would be slightly higher. With the large plants to which I refer in my paper, these figures would be nearly doubled.

I gather from the summary I have seen of Mr. Griffiths' paper that he is sceptical as to the value of the expansion engine. His comparisons, however, appear to be based on small plants for producing liquid only, and that of a low oxygen content. These are the conditions where an expansion engine shows up to least advantage. In practice the larger the plant the more efficient the expansion engine system becomes. Furthermore, the low initial pressure of the Claude apparatus, and other contingent advantages to which I refer in my paper, are important points which stand to the credit of the expansion engine.

There is, no doubt, scope for further improvement in the thermal efficiency of the liquid air method of producing both oxygen and nitrogen, and the Jeffries-Norton process to which I refer has the merit of being an effort in that direction, but to obtain higher thermal efficiency without a counterbalancing loss in mechanical efficiency is a difficult problem. To obtain a complete separation of the constituents of liquid air in one apparatus as suggested by Mr. Maxted is an even more difficult problem, and I agree with Mr. Swinburne that it will never be commercially possible to separate all the oxygen and nitrogen even in a state of commercial purity in the same rectification column.

The remarks on my paper by Dr. Richard Linde do not call for much comment. The energy consumption for large plants given by him is virtually in agreement with the figures which I give in my paper, although for plants of medium capacity Dr. Linde claims better efficiency than we have been able to obtain. However, in the absence of more data I am not able to offer any useful criticism.

As regards the quantity of oxygen distributed in cylinders annually in Germany, the estimate of upwards of 600,000,000 cubic feet which I give in the end of my paper is based on a figure published by Dr. Linde himself less than a year ago, and that gave an annual output in cylinders throughout Germany of 706,000,000 cubic feet. If within a period of less than twelve months the output of oxygen has nearly doubled in Germany, the fact is a striking indication of industrial activity in that country.

The comparison of the oxygen outputs in various countries which I give in my paper is based on the actual sales of the gas in cylinders, and not on plant capacities. I did not include private plants for the production of oxygen, of which there is now a considerable number in this country. The annual output from such plants obviously depends on the extent to which they are worked, and Dr. Linde's estimate of output in that connection must be purely conjectural.

**Mr. Georges Claude** (*communicated reply; translated*): I beg to offer a few remarks on some points touched upon during the discussion.

Dr. Harker has pointed out that he has, in the various installations of gas liquefaction which utilise external expansion—and particularly in installations using my apparatus—never seen that the energy recovered serves for any further purpose except to drive a dynamo and to heat up resistances. The use of a dynamo is very convenient; with the aid of an amperemeter and a voltmeter we can easily watch the working of the dynamo and consequently of the expansion engine, and that is important for the operation of the oxygen or nitrogen liquefier. It would certainly be easy to make the current generated do something more useful than heating the works, in spite of the fluctuations of the electric potential which the regulation of the apparatus may cause; but with small apparatus, in which the energy cost is small compared to the total cost of the oxygen, there is in general little inducement for this utilisation.

One must not conclude, however, that in these conditions the advantage of making use of an expansion engine would vanish. The main point is indeed not that the energy of expansion can be made to supply part of the energy needed for the compression; for owing to the low temperature at which the engine works and to the low efficiency of the apparatus, this energy portion will only be small. The chief object of the intervention of the expansion engine is that the mechanical energy which it liberates has its exact counterpart in the supplement of cold produced.

All the same I agree, of course, with Dr. Harker that we should not waste this energy in powerful plants when the price of the oxygen must be kept low. I should say in this connection, that in the pre-war installation at Ougrée, in Belgium, for enriching blast-furnace air with oxygen, we sent the energy of the expansion of the three apparatus used, each of 200 $m.^3$ of oxygen per hour, directly back to the pulley of the compressors. In a modified way this arrangement will be adopted in the two apparatus of 500 $m.^3$ each, which we are now putting up at Boulogne-sur-Seine.

Finally, in my new apparatus for the extraction of hydrogen from coke-oven gas, now planned for units of 2000 $m.^3$ of hydrogen per hour, this energy will serve for compressing the nitrogen required for the lubrication. Dr. Harker will thus soon be satisfied as to the question he has raised; for I firmly believe with him that the too long delayed time of big applications of oxygen and hydrogen will soon come, and large-scale apparatus will then be the rule.

With respect to the just-mentioned Ougrée plant I should add that if those experiments had not been stopped by the war at their beginning, they would probably have been a success. If I may judge from the first results, I believe I may assert, though precise figures were not obtained, that such installations must pay and that they could therefore be renewed without any risk. I wish that this assurance would induce some enterprising company to resume, as soon as possible, experiments which will perhaps result in a complete revolution of the metallurgical industry. I personally think that the most tempting promise of this use of oxygenated air would be the disappearance of the cumbrous iron structures of the heat interchangers.

There is one further remark to be made regarding this point. Although an only slightly-oxygenated air is required for this application, I consider that it would be a mistake to produce this slightly-enriched air directly in the separator. We had better make use of the fact that we have brought the air to be treated to the very low temperature which is required to extract all the oxygen in an almost pure state, and we then reduce the oxygen percentage to the desired weak concentration by the addition of air, the oxygen of which will attach itself to the manufactured oxygen without further cost.

As regards the integral separation of the air into pure oxygen and pure nitrogen, discussed by Dr. Maxted and by the Chairman, Mr. Swinburne, I think that the presence of argon is the greatest obstacle to this separation.

The volatility of argon lies between those of oxygen and of nitrogen. In order to eliminate the argon from the one of the two gases which we particularly need to have in pure condition, this argon must be driven into the second constituent with the aid of a portion of the first gas, and that portion will be lost and contaminate the other gas. We should provide for this argon a special exit from the apparatus, intermediate between those for the oxygen and nitrogen. That is what I have been trying to do, and so has Linde, and in this way the argon which is produced is now used in large amounts in the electric lamp industry. But we have only succeeded in recovering a fraction of the argon, and the success is only partial in so far as the better separation of oxygen and nitrogen is concerned.

I pass to the courteous observations contributed by Dr. Linde with respect to the consumption of energy in our respective processes. I thank Mr. Murray for what he was good enough to say; I acknowledge that the figures given by Dr. Linde do not differ much from those actually obtained in my apparatus. I should add, however, that more perfect realisation of the expansion, the recovery of the energy which I have already referred to, a better heat interchange and several other details will probably enable me to exceed 1·2 m.$^3$ of a 98 per cent. oxygen in the two plant of 500 m.$^3$ now being constructed for our Boulogne plant.

As regards our respective hydrogen processes, I also believe that the difference in the energy consumption is, in the case of water gas, greater than Dr. Linde has calculated. To compress 2100 m.$^3$ of water gas to 20 atmospheres requires only 400 h.p., the compression to 20 atmospheres of 1000 m.$^3$ of hydrogen 190 h.p., and the manufacture of 350 m.$^3$ of nitrogen requires 100 h.p.: as regards the compression of the nitrogen wanted for lubrication, I have said that the expansion will easily supply that energy. There would then be a total of a little less than 700 h.p. against the 900 h.p. of the Linde process.

I should like moreover to repeat that I have never estimated that the liquefaction of water gas could economically stand against the process of the Badische Anilin Fabrik. That liquefaction of water gas has served me merely as a preparatory step in attaining the much more interesting liquefaction of coke-oven gas. There the process of the Badische is impotent since methane is not catalysable. I should add that I have never been troubled by "water-hammer" effects, and that the nitrogen present in the hydrogen could not be deleterious in the special application for the ammonia synthesis with which my process has been combined.

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